

WYDZIAŁ INŻYNIERII PRODUKCJI I TECHNOLOGII MATERIAŁÓW
KATEDRA ZARZĄDZANIA PRODUKCJĄ
POLITECHNIKA CZĘSTOCHOWSKA

*Analiza możliwości zagospodarowania uciążliwych dla
środowiska produktów termicznego przetwarzania odpadów
kalorycznych do opalania hutniczych pieców grzewczych*

Rozprawa doktorska

mgr inż. Magdalena Skrzyniarz

Promotor: dr hab. inż. Paweł Niegodajew, prof. PCz.

Promotor pomocniczy: dr inż. Sławomir Morel

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Składam serdeczne podziękowania

Promotorowi, Panu Profesorowi Pawłowi Niegodajewowi,
Promotorowi pomocniczemu, Panu dr Sławomirowi Morelowi,
Kolegom i Koleżankom z Politechniki Częstochowskiej, Politechniki Śląskiej
oraz z Akademii Górniczo-Hutniczej w Krakowie
Mojemu mężowi i synowi,
za wsparcie, pomoc oraz wiarę we mnie podczas realizacji niniejszej rozprawy.



Dorobek naukowy autora

Artykuły, na których opiera się rozprawa doktorska:

- A1. **SKRZYNIARZ Magdalena**, SAJDAK Marcin, ZAJEMSKA Monika, IWASZKO Józef, BINIEK-POSKART Anna, SKIBIŃSKI Andrzej, MOREL Sławomir, NIEGODAJEW Paweł, *Plastic Waste Management towards Energy Recovery during the COVID-19 Pandemic: the Example of Protective Face Mask Pyrolysis*, *Energies*, 15(7), 2629 (2022), 140 pkt. IF: 3,0.

Wkład autora: Współtwórca koncepcji, opracowanie metodologii, przeprowadzenie części symulacji komputerowych (zamodelowanie dokładnego składu chemicznego gazowych produktów pirolizy), udział w analizie teoretycznej, dyskusja uzyskanych wyników, częściowe przygotowanie manuskryptu, przygotowanie grafik, udział w przygotowaniu odpowiedzi dla recenzentów.

- A2. ZAJEMSKA Monika, MAGDZIARZ Aneta, IWASZKO Józef, **SKRZYNIARZ Magdalena**, POSKART Anna, *Numerical and Experimental Analysis of Pyrolysis Process of RDF Containing a High Percentage of Plastic Waste*, *Fuel*, 320, 123981 (2022), 140 pkt. IF: 6,7.

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- A3. ZAJEMSKA Monika, SAJDAK Marcin, IWASZKO Józef, **SKRZYNIARZ Magdalena**, BINIEK-POSKART Anna, SKIBIŃSKI Andrzej, MAROSZEK Artur, *The Role of Calorific Waste in Transformation of Iron and Steel Industry Towards Sustainable Production*, *Resource, Conservation and Recycling*, vol. 191, 106899 (2023), 140 pkt. IF: 11,2.



Wkład autora: Udział w analizie teoretycznej, skonstruowanie wniosków, częściowe przygotowanie manuskryptu, przygotowanie grafik.

- A4. BINIEK-POSKART Anna, SAJDAK Marcin, **SKRZYNIARZ Magdalena**, RZĄCKI Jakub, SKIBIŃSKI Andrzej, ZAJEMSKA Monika, *The Application of Lignocellulosic Biomass Waste in the Iron and Steel Industry in the Context of Challenges Related to the Energy Crisis*, *Energies*, 16(18), 6662 (2023), 140 pkt. IF: 3,0.

Wkład autora: Współtwórca koncepcji, udział w analizie teoretycznej, dyskusja uzyskanych wyników, częściowe przygotowanie manuskryptu, przygotowanie grafik, udział w przygotowaniu odpowiedzi dla recenzentów.

- A5. **SKRZYNIARZ Magdalena**, SAJDAK Marcin, ZAJEMSKA Monika, BINIEK-POSKART Anna, IWASZKO Józef, SKIBIŃSKI Andrzej, *Possibilities of RDF Pyrolysis Products Utilization in the Face of the Energy Crisis*, *Energies*, 16(18), 6695 (2023), 140 pkt. IF: 3,0.

Wkład autora: Współtwórca koncepcji, udział w analizie teoretycznej, dyskusja uzyskanych wyników, częściowe przygotowanie manuskryptu, przygotowanie grafik, udział w przygotowaniu odpowiedzi dla recenzentów.

- A6. **SKRZYNIARZ Magdalena**, SAJDAK Marcin, BINIEK-POSKART Anna, SKIBIŃSKI Andrzej, KRAKOWIAK Marlena, PIOTROWSKI Andrzej, KRASOŃ Patrycja, ZAJEMSKA Monika, *Methods and Validation Techniques of Chemical Kinetics Models in Waste Thermal Conversion Processes*, *Energies*, 17(13), 3067 (2024), 140 pkt. IF: 3,0.

Wkład autora: Współtwórca koncepcji, udział w analizie teoretycznej, dyskusja uzyskanych wyników, częściowe przygotowanie manuskryptu, przygotowanie grafik, udział w przygotowaniu odpowiedzi dla recenzentów.

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- A7. **SKRZYNIARZ Magdalena, RZĄCKI Jakub**, *Analiza mechanizmów chemicznych powstawania uciążliwych dla środowiska produktów spalania gazu z pirolizy odpadów*, *Przemysł Chemiczny*, 103(9), 979-983 (2024), 70 pkt. IF: 0,5.

Wkład autora: Przeprowadzenie symulacji komputerowych (zamodelowanie dokładnego składu chemicznego gazowych produktów pirolizy), analiza teoretyczna, dyskusja uzyskanych wyników, przygotowanie manuskryptu, przygotowanie grafik, udział w przygotowaniu odpowiedzi dla recenzentów.

- A8. **SKRZYNIARZ Magdalena, MOREL Sławomir, RZĄCKI Jakub**, *Prediction of chemical composition of gas combustion products from thermal waste conversion*, *Processes*, 12(12), 2728 (2024), 70 pkt, IF: 2,8.

Wkład autora: Współtwórca koncepcji, opracowanie metodologii, przeprowadzenie symulacji komputerowych (zamodelowanie dokładnego składu chemicznego gazowych produktów pirolizy), analiza teoretyczna, dyskusja uzyskanych wyników, częściowe przygotowanie manuskryptu, przygotowanie grafik, udział w przygotowaniu odpowiedzi dla recenzentów.

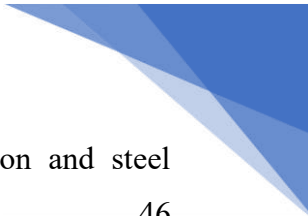
- A9. **SKRZYNIARZ Magdalena, SAJDAK Marcin, BINIEK-POSKART Anna, SKIBIŃSKI Andrzej, MAROSZEK Artur, NIEGODAJEW Paweł, ZAJEMSKA Monika**, *Economic Benefits for the Metallurgical Industry from Co-Combusting Pyrolysis Gas from Waste*, *Energy*, 133782 (2024), 200 pkt. IF: 9,0.

Wkład autora: współtwórca koncepcji, opracowanie metodologii, udział w analizie teoretycznej, wykonanie analizy ekonomicznej, dyskusja uzyskanych wyników, częściowe przygotowanie manuskryptu, przygotowanie grafik, udział w przygotowaniu odpowiedzi dla recenzentów.



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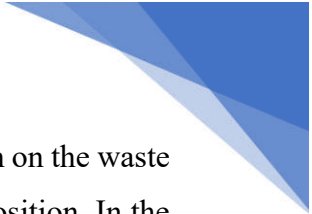


Abstract of the doctoral thesis

The process of waste pyrolysis is a promising method of thermal conversion, which can be used in the steel industry to reduce the operating costs of the plant. In this doctoral dissertation, entitled "*Analysis of the possibilities of utilizing environmentally harmful products of thermal conversion of calorific waste for firing metallurgical heating furnaces*", the possibility of thermal conversion of various types of waste is examined, using its products for co-combustion with natural gas, in a metallurgical heating furnace. The work focuses on the analysis of the physicochemical properties of selected waste and on the selection of appropriate parameters of the pyrolysis process, so that the gas fraction yield is as high as possible. In my work, I focus on selecting the appropriate waste, which, when subjected to the pyrolysis process, will demonstrate the best technical properties (appropriate calorific value) and will be an alternative, possible to be used on a large scale, to reduce the dependence of the metallurgical industry on fossil fuels, the reserves of which will one day run out. The first part of the doctoral dissertation presents the motivation for the undertaken topic, the thesis and the utilitarian goal of the work, explaining why diversification of energy sources in the steel industry will contribute to the decarbonization of the steel industry and bring energy-intensive industries closer to the transition from a linear economy to a circular economy. Then I focus on the current methods of using pyrolysis gas. In the next part, I describe the directions of energy use from waste on the example of Poland and the possibilities of waste management and thermal conversion products in the steel industry, taking into account the need to decarbonize the steel industry.

The chapter on methodology describes in detail the applied research techniques and computer simulations, clearly showing what tests and simulations were performed at each stage of the research.

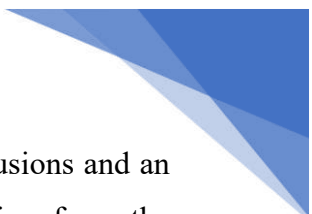
The main part of the work analyzes a number of wastes, namely: pine waste, alder waste, medical waste - protective mask, rubber waste - granulate from passenger car tires, furniture industry waste - MDF boards and RDF waste. Comparing the results of simulations and calculations of the calorific value of pyrolysis gases produced from the above-mentioned materials, RDF waste was selected for further research due to its high calorific value (20.5 MJ/m^3) of the obtained gas (below 35 MJ/m^3 – technological conditions of burners) and high availability throughout the country. In the further part of the work, pyrolysis gas from RDF was considered from the perspective of its co-



combustion with natural gas in a metallurgical heating furnace. The research on the waste was extended to a detailed technical analysis and analysis of the ash composition. In the next step, a pyrolysis experiment was carried out in the laboratory of the Faculty of Materials Engineering and Industrial Computer Science (Department of Thermal Technology and Environmental Protection) of the AGH University of Science and Technology in Krakow. Then, all products obtained during the pyrolysis process (solid, liquid and gaseous fractions) were collected and analyzed. The best results in gas fraction yield and the highest calorific value were obtained for the pyrolysis temperature of 800°C and the sample residence time of 3 min. The gas fraction yield reached over 46%, and the calorific value of the obtained gas was 22.5 MJ/m³. The tested condensates were also characterized by a high calorific value of over 30 MJ/kg. Fourier transform infrared spectroscopy (FTIR) analysis of the obtained chars showed a lack of clear absorption band ranges in the solid fraction from pyrolysis at 800°C, which indicates the degradation of most bonds during pyrolysis. The next part of the paper describes the concept of incorporating a pyrolysis reactor into the existing technological sequence of the pusher furnace in the thick plate department of one of the Polish steelworks. The description provides technical parameters of the installation. It was assumed that the pyrolysis reactor with a capacity of 1000 kg/h would produce over 50% of the input mass of natural gas together with the uncondensed liquid fraction (process temperature 900°C), which would be directed directly to the pusher furnace burners. The estimated value of the investment is EUR 5,300,000 of capital expenditure (CAPEX).

Then, using the Ansys Chemkin PRO (v. 2021 R1) computer program, computer simulations were performed, predicting the composition of exhaust gases generated after co-combustion of natural gas with pyrolysis gas. The analysis showed a similarity in the composition of exhaust gases. Co-combustion of both gases did not increase the share of undesirable compounds in the exhaust gases from co-combustion, compared to the exhaust gases from the combustion of pure natural gas.

For the above solution, an economic analysis was carried out using the net present value (NPV) method, which showed the profitability of the investment. The monthly savings that the steelworks will experience due to the reduced consumption of natural gas will amount to PLN 200 by 450 thousand euros per month, depending on the efficiency of the furnace. The analysis showed a return on investment within 3-4 years of its operation.



The dissertation ends with a summary of the most important conclusions and an indication of the potential economic and environmental benefits resulting from the implementation of the solution presented above.

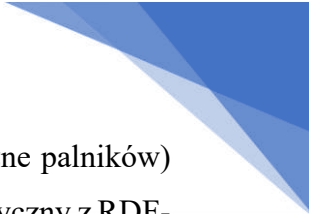
Streszczenie rozprawy doktorskiej

Proces pirolizy odpadów jest obiecującą metodą termicznego przekształcania, możliwą do wykorzystania w przemyśle stalowym, do obniżenia kosztów funkcjonowania zakładu. W tej rozprawie doktorskiej, zatytułowanej „*Analiza możliwości zagospodarowania uciążliwych dla środowiska produktów termicznego przetwarzania odpadów kalorycznych do opalania hutniczych pieców grzewczych*” badana jest możliwość termicznego przetwarzania różnego rodzaju odpadów, z wykorzystaniem jej produktów do współpalania z gazem ziemnym, w hutniczym piecu grzewczym. Praca koncentruje się na analizie właściwości fizykochemicznych wybranych odpadów oraz na doborze odpowiednich parametrów procesu pirolizy, aby uzysk frakcji gazowej był jak największy. W pracy skupiam się nad wytypowaniem odpowiedniego odpadu, który poddany procesowi pirolizy wykaże najlepsze właściwości techniczne (odpowiednia kaloryczność) oraz będzie alternatywą, możliwą do zastosowania na szeroką skalę, aby ograniczyć zależność przemysłu hutniczego od paliw kopalnych, których rezerwy kiedyś się skończą.

Pierwsza część rozprawy doktorskiej przedstawia motywację podjętego tematu, tezę i cel użyteczny pracy, wyjaśniając, dlaczego dywersyfikacja źródeł wytwarzania energii w przemyśle stalowym, przyczyni się do jego dekarbonizacji i zbliży energochłonne gałęzie przemysłu do przejścia z gospodarki liniowej na gospodarkę o obiegu zamkniętym. Następnie skupiono się na dotychczasowych sposobach wykorzystania gazu pirolitycznego. W kolejnej części opisano kierunki energetycznego wykorzystania odpadów na przykładzie Polski oraz możliwości zagospodarowania odpadów i produktów termicznego przetwarzania w przemyśle stalowym, z uwzględnieniem konieczności dekarbonizacji tego przemysłu.

Rozdział poświęcony metodyce szczegółowo opisuje zastosowane techniki badawcze i metody numeryczne, jasno wskazując jakie badania i symulacje zostały wykonane na poszczególnych etapach pracy.

W głównej części pracy przeanalizowano różne rodzaje odpadów, a mianowicie: odpady sosnowe, odpady olchowe, odpady medyczne – maseczkę ochronną, odpady gumowe – granulaty z opon samochodów osobowych, odpady przemysłu meblarskiego – płyty MDF oraz odpady typu RDF. Porównując wyniki symulacji i obliczeń wartości opałowej gazów pirolitycznych powstałych z ww. materiałów, do dalszych badań wytypowano odpad RDF ze względu na wysoką wartość opałową uzyskanego gazu,

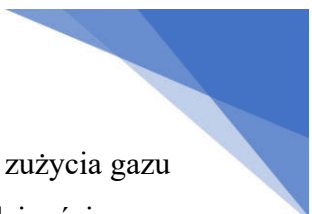


wynoszącą 20,5 MJ/m³ (poniżej 35 MJ/m³ – uwarunkowania technologiczne palników) oraz dużą dostępność w skali całego kraju. W dalszej części pracy gaz pirolityczny z RDF-u był rozpatrywany pod kątem jego współspalania z gazem ziemnym w hutniczym piecu grzewczym. Badania RDF rozszerzono o analizę techniczną i analizę składu popiołu. W kolejnym etapie badań przeprowadzono eksperymenty laboratoryjne rozkładu termicznego RDF na drodze pirolizy. Badania zrealizowano w laboratorium Wydziału Inżynierii Materiałowej i Informatyki Przemysłowej (Katedra Techniki Ciepłej i Ochrony Środowiska) Akademii Górniczo-Hutniczej w Krakowie. Następnie zebrano i poddano analizie wszystkie uzyskane podczas procesu pirolizy produkty, a mianowicie gaz pirolityczny, karbonizat i kondensat. Największy uzysk frakcji gazowej o najwyższej wartości opałowej uzyskano dla temperatury pirolizy 800°C i czasu przebywania próbki 3 minuty. Uzysk frakcji gazowej osiągnął ponad 46%, a wartość opałowa gazu pirolitycznego wynosiła 22,51 MJ/m³. Badane kondensaty również charakteryzowały się wysoką wartością opałową, wynoszącą ponad 30 MJ/kg. Analiza metodą spektroskopii w podczerwieni z transformacją Fouriera (FTIR) uzyskanych karbonizatów wykazała brak wyraźnych zakresów pasm absorpcji we frakcji stałej pochodzącej z pirolizy w temperaturze 800°C, co świadczy o zdegradowaniu większości wiązań w czasie pirolizy.

W kolejnej części pracy opisano koncepcję włączenia reaktora pirolitycznego do istniejącego ciągu technologicznego pieca przepychowego, na wydziale blach grubych jednej z polskich hut stali. W opisie zostały podane parametry techniczne instalacji. Do obliczeń przyjęto założenie, że reaktor pirolityczny o wydajności 1000 kg/h będzie dostarczał ponad 50% , w stosunku do masy wejściowej, gazu pirolitycznego wraz z niekondensowalną frakcją ciekłą (temperatura procesu 900°C), który zostanie skierowany bezpośrednio do palników pieca przepychowego. Oszacowana wartość inwestycji to 5 300 000 euro wydatków kapitałowych (CAPEX).

Następnie wykorzystując program komputerowy Chemkin v. 2021 przeprowadzono symulacje komputerowe, przewidując skład gazów spalinowych powstałych po współspalaniu gazu ziemnego z gazem pirolitycznym. Analiza wykazała, że współspalanie obydwu gazów nie wpłynęło na podwyższenie udziału niepożądanych związków w spalinach, w porównaniu do gazów spalinowych pochodzących ze spalania czystego gazu ziemnego.

Dla powyższego rozwiązania została przeprowadzona analiza ekonomiczna metodą wartości bieżącej netto (NPV), która wykazała opłacalność inwestycji.



Miesięczne oszczędności, które poniesie huta w związku ze zmniejszeniem zużycia gazu ziemnego wyniosą od 200 do 450 tys. euro miesięcznie, w zależności od wydajności pracy pieca. Analiza wykazała zwrot inwestycji w ciągu 3-4 lat jej funkcjonowania.

Rozprawa kończy się podsumowaniem i wnioskami, ze wskazaniem potencjalnych korzyści ekonomicznych i środowiskowych wynikających z implementacji zaproponowanego rozwiązania.

1. Wprowadzenie

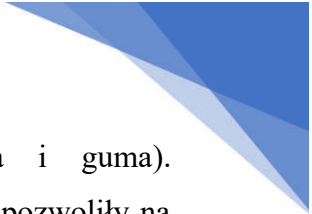
1.1. Motywacja

Zaproponowana tematyka wychodzi naprzeciw problemom, z jakimi boryka się polski przemysł hutniczy i tzw. branża odpadowa, zwłaszcza w zakresie wysokiej energochłonności

i negatywnego wpływu na środowisko naturalne. Zaproponowane w pracy badania wpisują się również w wyzwania, przed którymi stoi Polska, w związku z obowiązującymi od 1 stycznia 2016 r. przepisami rozporządzenia Ministra Gospodarki, zakazującymi składowania wysokokalorycznych odpadów, tzn. takich, których ciepło spalania wynosi powyżej 6 MJ/kg suchej masy [1]. Obecnie, znaczna ich część przetwarzana jest na paliwo RDF (Refused Derived Fuel), które pod warunkiem, że spełnia wytyczne postawione przez odbiorców (głównie cementownie) trafia do spalania z odzyskiem energetycznym [2]. W skali kraju nie jest możliwe przerobienie wszystkich odpadów na paliwo RDF, a w konsekwencji brak jest możliwości ich maksymalnego wykorzystania pod względem energetycznym. Alternatywą dla spalarni może być technologia pirolizy oraz zgazowania odpadów, w wyniku których można uzyskać gaz, którego skład zależy nie tylko od warunków prowadzenia procesu, ale przede wszystkim od rodzaju spalanych odpadów [3]. Na chwilę obecną najbardziej problematyczną pod względem termicznego przetwarzania grupą odpadów są odpady z tworzyw sztucznych oraz odpady gumowe i tekstylne. Skład chemiczny zarówno gazu pirolitycznego, jak i gazu ze zgazowania odpadów może być mocno zróżnicowany, co będzie się przekładać na wpływ ich spalania na środowisko.

W niniejszej rozprawie gaz pirolityczny był badany jako alternatywa dla gazu ziemnego, w kontekście jego współspalania, wypełniając tym samym lukę badawczą w zakresie jego zastosowania w przemyśle żelaza i stali, szczególnie w piecach grzewczych.

Analiza literatury jednoznacznie wskazała, że żadne z dotychczasowych badań nie dotyczyły wykorzystania gazu pirolitycznego do opalania pieców grzewczych w tym sektorze. Zaproponowana koncepcja obejmuje ponadto pionierskie podejście do wykorzystania energii odpadowej pochodzącej z opalania pieców grzewczych do ogrzewania reaktora na potrzeby wytwarzania gazu pirolitycznego. Dodatkowo, przeprowadzone badania wpisują się w aktualne wyzwania środowiskowe, poprzez adaptację procesu pirolizy na potrzeby zagospodarowania problematycznych dla



środowiska odpadów kalorycznych (tworzywa sztuczne, tekstylia i guma). Przeprowadzone symulacje komputerowe oraz badania materiałoznawcze pozwoliły na ocenę wielkości emisji szkodliwych dla środowiska gazowych produktów pirolizy powstałych w wyniku jego współspalania z gazem ziemnym.

Zaproponowane w pracy rozwiązanie oprócz korzyści środowiskowych prowadzi do znacznych oszczędności gazu ziemnego, dzięki współpalaniu z gazem pirolitycznym, osiągając użyteczny cel pracy. Uzyskane wyniki badań wykazały, że już niewielki udział gazu pirolitycznego w mieszance paliwowej skutkuje znacznym zmniejszeniem zużycia gazu ziemnego, biorąc pod uwagę wysokie zapotrzebowanie na energię w procesie ogrzewania w produkcji stali. Prowadzi to nie tylko do redukcji kosztów, ale także do poprawy efektywności energetycznej.

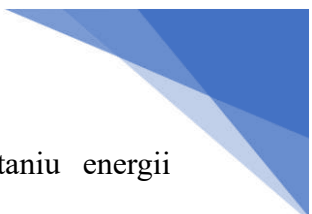
Propagowanie zasad zrównoważonego rozwoju i wdrażanie proekologicznych rozwiązań stanowi atut w działaniach marketingowych przedsiębiorstwa i wpisuje się w transformację przemysłu hutniczego (dekarbonizację przemysłu hutniczego).

Zaproponowana koncepcja włączenia gazu pirolitycznego do opalania hutniczych pieców grzewczych, z jednoczesnym wykorzystaniem ciepła odpadowego, wypełnia lukę zarówno w badaniach naukowych, jak i w praktyce przemysłowej, podkreślając potencjalne korzyści ekonomiczne i środowiskowe wynikające ze zmniejszenia zależności od gazu ziemnego w produkcji stali.

1.2. Teza i cel pracy

Głównym celem pracy jest szczegółowa analiza mechanizmów chemicznych odpowiedzialnych za bezpieczne, zarówno pod względem technologicznym, jak i środowiskowym, zagospodarowanie gazów uzyskiwanych w czasie termicznego przekształcania odpadów do opalania hutniczych pieców grzewczych. W szczególności skupiono się na doborze mieszanki paliwowej tj. gazu ziemnego i pirolitycznego podawanej do pieca grzewczego, w kontekście środowiskowym, technologicznym i ekonomicznym.

W ramach rozprawy doktorskiej opracowano koncepcję implementacji reaktora pirolitycznego, w istniejący ciąg technologiczny linii do walcowania blach grubych, w piecu przepychowym, zlokalizowanym w jednej z polskich Hut Stali, w taki sposób aby osiągnąć **cel użyteczny**, mianowicie: obniżenie kosztów produkcji w przedsiębiorstwie hutniczym poprzez zagospodarowanie gazu powstałego w wyniku termicznego przetwarzania problematycznych odpadów kalorycznych, takich jak:



tworzywa sztuczne, tekstylia i guma, przy jednoczesnym wykorzystaniu energii pochodzącej ze spalin do podgrzewania reaktora pirolitycznego.

2. Przegląd literaturowy

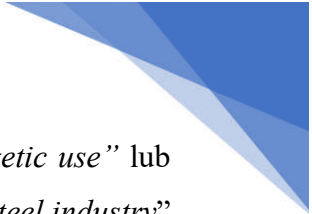
Podjęta w pracy problematyka wpisuje się w zagadnienie transformacji energetycznej przemysłu hutniczego. Porozumienie klimatyczne z Paryża (2015 r.) oraz Europejski Zielony Ład (2019 r.) narzuciły konieczność redukcji emisji CO₂ do roku 2030, do poziomu zerowego netto. Do roku 2050 Unia Europejska zaplanowała konieczność osiągnięcia Neutralności Klimatycznej Europy oraz przejście europejskiej gospodarki z liniowej (GL) na gospodarkę o obiegu zamkniętym (GOZ). Wszystkie wymienione uwarunkowania legislacyjne mają wpływ na obecną sytuację energetyczną na świecie. Nie tylko na branżę elektrociepłowniczą, ale także energochłonne gałęzie przemysłu, takie jak przemysł żelaza i stali, ma wpływ wiele czynników, a w szczególności: trudna sytuacja geopolityczna (kryzys energetyczny) i związane z nią ograniczenia w dostępności paliw konwencjonalnych, wzrost cen paliw, a także wzrastające opłaty za prawo do emisji CO₂. Aby zapewnić nieprzerwaną produkcję i zredukować jej koszty, przemysł metalurgiczny musi zdywersyfikować dostawy paliwa gazowego, zwracając się w stronę bardziej przyszłościowych i przyjaznych środowisku alternatyw. Jedną z nich jest wykorzystanie potencjału odpadów, które poddane termicznemu przetwarzaniu [4] mogą dostarczyć cennych produktów, a w szczególności wysokokalorycznego gazu [5,6].

Współczesne systemy gospodarki odpadami opierają się na metodach termicznego przetwarzania, w szczególności na spalaniu [7]. Oprócz spalania odpady poddawane są również przetworzeniu przy użyciu innych procesów, takich jak piroliza [8] i zgazowanie [9]. Oba te procesy wpisują się w koncepcję gospodarki o obiegu zamkniętym (circular economy) [10,11], która zakłada stałe wykorzystanie i przetwarzanie odpadów na nowe surowce [12]. Dlatego też bardziej pożądanym działaniem jest utylizacja odpadów za pomocą metod termicznego przetwarzania [13,14].

Zaproponowane w rozprawie doktorskiej podejście do energetycznego wykorzystania gazu pirolitycznego, polegające na współspalaniu tego gazu z gazem ziemnym w hutniczym piecu grzewczym typu przepychowego, wykazuje cechy innowacyjności gdyż do tej pory nie zostało opisane przez innych badaczy.

2.1. Analiza zagadnienia i wykorzystanie gazu pirolitycznego

Do analizy stanu literaturowego wykorzystano bazę Scopus, ze względu na największą liczbę indeksowanych czasopism (ponad 16 tys.). Wytypowanie publikacji zostało przeprowadzone za pośrednictwem „Scopus Article Database”. Wyszukiwanie



obejmowało słowa kluczowe: „*pyrolysis gas*” lub „*pyrolytic gas*”, „*energetic use*” lub „*energy*” oraz „*iron and steel*” lub „*steel and iron*” lub „*metallurgy*” lub „*steel industry*” (w tytułach, słowach kluczowych i abstraktach), tak aby wytypować jedynie artykuły, które są związane z podjętą w rozprawie tematyką. W wyniku wyszukiwania znaleziono 9 artykułów w czasopismach indeksowanych, spełniające założone kryteria. Część z odnalezionych artykułów (5 pozycji) dotyczyła tematyki około metalurgicznej, mianowicie: recyklingu materiałowego, wykorzystania biowęgla pochodzącego z procesu pirolizy jako środka redukcyjnego w procesie produkcji żelaza [15–19], dwie prace dotyczyły procesu pirolizy: wykorzystania pirolizy i zgazowania węgla niskostopowego do wytworzenia gazu bogatego w wodór, w celu uzyskania bezpośrednio zredukowanego żelaza (metoda DRI) [20] oraz produkcji energii elektrycznej w procesie pirolizy [21]. Dwa z spośród wszystkich odszukanych artykułów dotyczyły tematyki zaproponowanej w niniejszej rozprawie i były mojego współautorstwa [22,23]. Dla zobrazowania zainteresowania tematem, dokonano ponownego wyszukiwania ograniczając słowa kluczowe do: „*pyrolysis gas*” lub „*pyrolytic gas*” i „*energetic use*” lub „*energy*” (wyszukiwanie ograniczone do abstraktu i języka artykułu tj. angielskiego). Wyniki dały 979 artykułów, spełniających założone kryteria wyszukiwania. Głównymi kierunkami, w jakich obecnie wykorzystywany jest gaz pirolityczny to produkcja energii elektrycznej oraz podtrzymywanie procesu pirolizy [24–28].

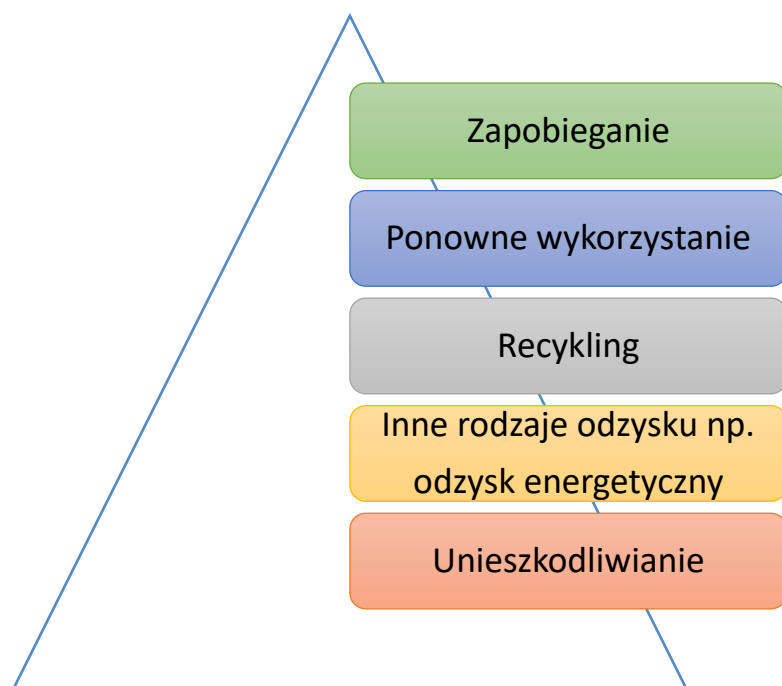
Jak pokazuje powyższa analiza, temat zastosowania produktów pirolizy na cele energetyczne był już szeroko zbadany, jednak nowatorska koncepcja zaproponowana w niniejszej pracy jest tematem praktycznie niezbadanym, innowacyjnym i nowatorskim.

Według bazy Scopus jest 979 publikacji, w których poruszono problemem pirolizy lecz wszystkie te artykuły dotyczyły szerokiego zakresu zastosowania tego procesu w różnych dziedzinach. Koncepcja wykorzystania pirolizy w hutnictwie do obniżania kosztów pracy pieca i utylizacji odpadów nie została omówiona w żadnym z ww. artykułów, co stanowiło istotny argument przy podjęciu decyzji o wyborze problematyki badawczej niniejszej rozprawy doktorskiej.

2.2. Kierunki energetycznego wykorzystania odpadów

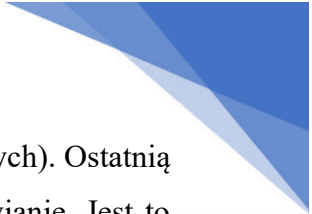
Odpady komunalne to zarówno odpady powstające w gospodarstwach domowych, jak i te, które nie zawierają w swoim składzie odpadów niebezpiecznych, ale są produkowane przez innych wytwórców odpadów, a ich skład i charakter jest podobny do odpadów pochodzących z gospodarstw domowych [29]. W Polsce obowiązuje

hierarchia postępowania z odpadami (rys. 1), według której w pierwszej kolejności należy dążyć do zapobiegania powstawania odpadów. Jeśli jest to niemożliwe, odpad należy ponownie wykorzystać. Jeśli ponowne wykorzystanie jest problematyczne, nieopłacalne lub niemożliwe należy odpady poddać recyklingowi materiałowemu. Jeśli żadne z powyższych rozwiązań nie jest możliwe, należy poddać odpady odzyskowi, np. energetycznemu. Jak już wcześniej wspomniano, od dnia 1 stycznia 2016 roku obowiązują przepisy rozporządzenia Ministra Gospodarki, zakazujące składowania odpadów wysokokalorycznych, tzn. takich, których ciepło spalania wynosi powyżej 6 MJ/kg suchej masy [1], skutkiem czego jest produkcja tzw. paliwa odpadowego (RDF - Refuse Derived Fuel). RDF [30,31] może być stosowane jako substytut konwencjonalnych paliw kopalnych w przemyśle cementowym [32,33] oraz do wytwarzania energii elektrycznej [34,35].



Rys. 1. Hierarchia postępowania z odpadami w Polsce (praca własna na podstawie [29])

Pozostałe odpady, które nie zostały poddane innym metodom odzysku są głównie przekształcane termicznie w spalarniach odpadów komunalnych, gdzie powstaje ciepło i energia elektryczna. Bio-odpady pochodzenia rolniczego mogą być przetwarzane w biogazowniach lub wykorzystywane do produkcji naturalnych nawozów [36,37]. Efektywność metod termicznego przetwarzania odpadów komunalnych jest zróżnicowana, co wynika ze zmiennej morfologii odpadów, zależnej np. od miejsca ich występowania [38]. Mimo to, spalanie odpadów w zakładach termicznego przetwarzania



jest dominującą metodą odzysku energii (dane GUS- Bank Danych Lokalnych). Ostatnią możliwością w hierarchii gospodarowania odpadów jest ich unieszkodliwianie. Jest to najmniej pożądana metoda ze wszystkich dostępnych.

2.3. Zagospodarowanie odpadów i produktów termicznego przetwarzania odpadów w przemyśle stalowym

Kluczowym wyzwaniem w kierunku globalnych działań mających na celu ograniczenie emisji gazów cieplarnianych i walką ze zmianami klimatycznymi jest dekarbonizacja przemysłu stalowego. Obecnie szacuje się, że branża hutnicza odpowiada za 7-8% globalnej emisji dwutlenku węgla [39]. Żelazo i stal są kluczowymi produktami, bez których funkcjonowanie innych branż nie byłoby możliwe. Z tego względu dekarbonizacja tego sektora jest niezwykle istotna.

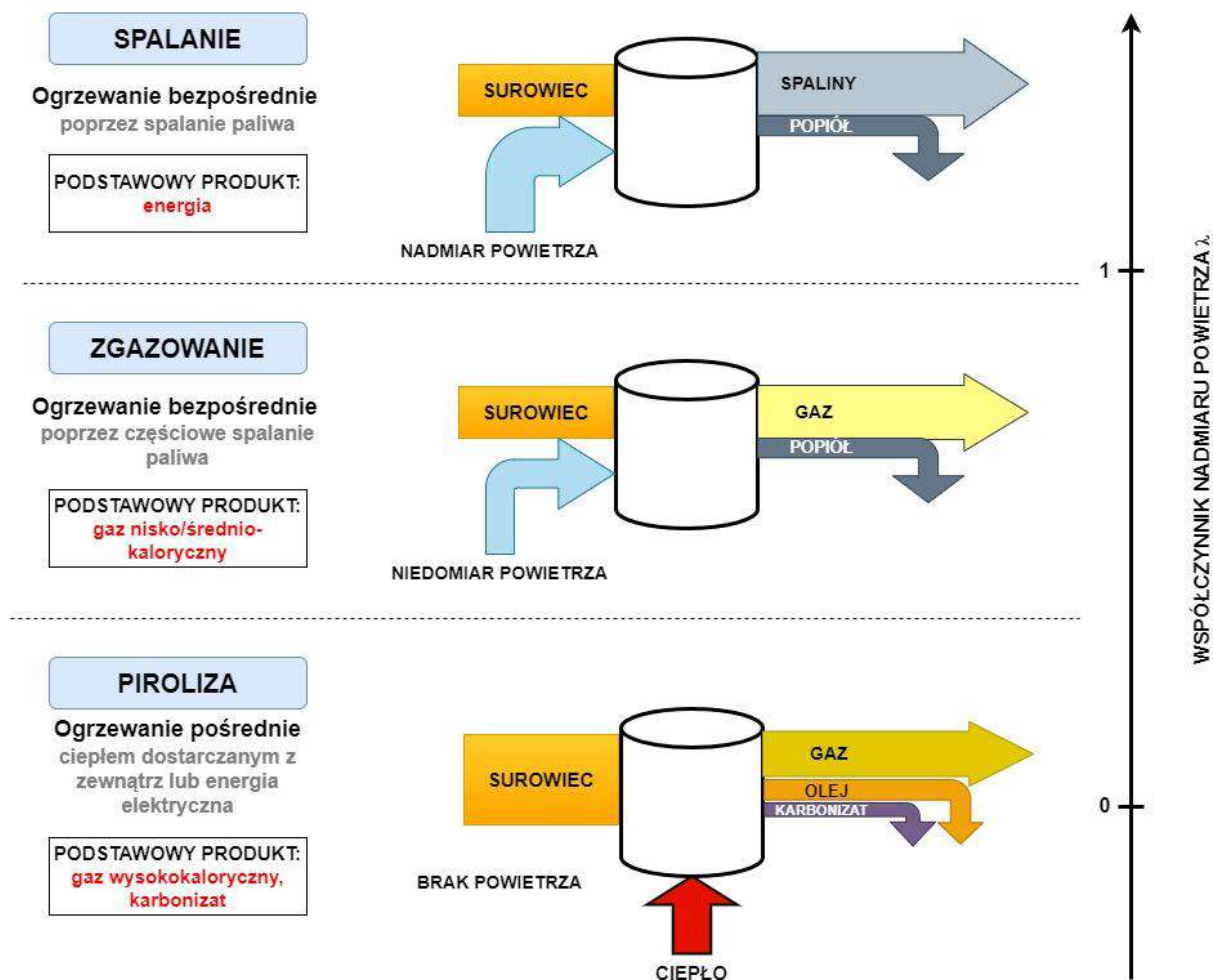
Działaniami w jakich upatruje się zmniejszenia emisji CO₂ i uniezależnienia się od paliw kopalnych są:

- zastępowanie koksu wodorem, jako reduktora w procesie produkcji stali [40],
- elektryfikacja pieców - zwiększenie stosowania technologii EAF (elektryczny piec łukowy – Electric Arc Furnance), zwłaszcza w połączeniu z energią elektryczną pochodzącą ze źródeł odnawialnych [41],
- wychwytywanie i składowanie CO₂ (CCS - Carbon Capture and Storage), pozwala na zmagazynowanie dwutlenku węgla, nie uwolnieniu go do atmosfery i wykorzystaniu w innych procesach [42],
- zwiększenie udziału recyklingu żelaza i stali, co bezpośrednio przełoży się na przejście z gospodarki liniowej na gospodarkę o obiegu zamkniętym.

Oprócz powyższych rozwiązań naukowcy pracują nad nowymi możliwościami, które pomogą w dekarbonizacji przemysłu. Jednym z nich jest stosowanie reduktorów pochodzenia biomasowego podczas produkcji stali, które będą odpowiadały za niższą emisję CO₂ [43–45]. Stosowanie biomasy w przemyśle hutniczym jest przedmiotem wielu badań, ale większość rozwiązań nie zostało do tej pory zaimplementowane w skali globalnej.

Pozytywnego wpływu na środowisko w kontekście dekarbonizacji upatruje się również w zagospodarowaniu odpadów, które po przekształceniu termicznym dają cenne produkty, które będzie można wykorzystać w przemyśle stalowym. Techniki termicznego przetwarzania takie jak: spalanie, piroliza i gazyfikacja stosowane są obecnie na całym świecie w różnych zakładach kogeneracyjnych do wytwarzania zarówno energii

elektrycznej, jak i ciepła [46]. Należy jednak zauważyć, że każdy z tych procesów wykazuje zmienność parametrów, w tym warunków atmosferycznych (obecności tlenu lub jego brak), temperatury roboczej, instalacji termicznej i innych czynników [47,48]. Na rysunku 2 przedstawiono porównanie różnych technik termicznego przetwarzania odpadów.

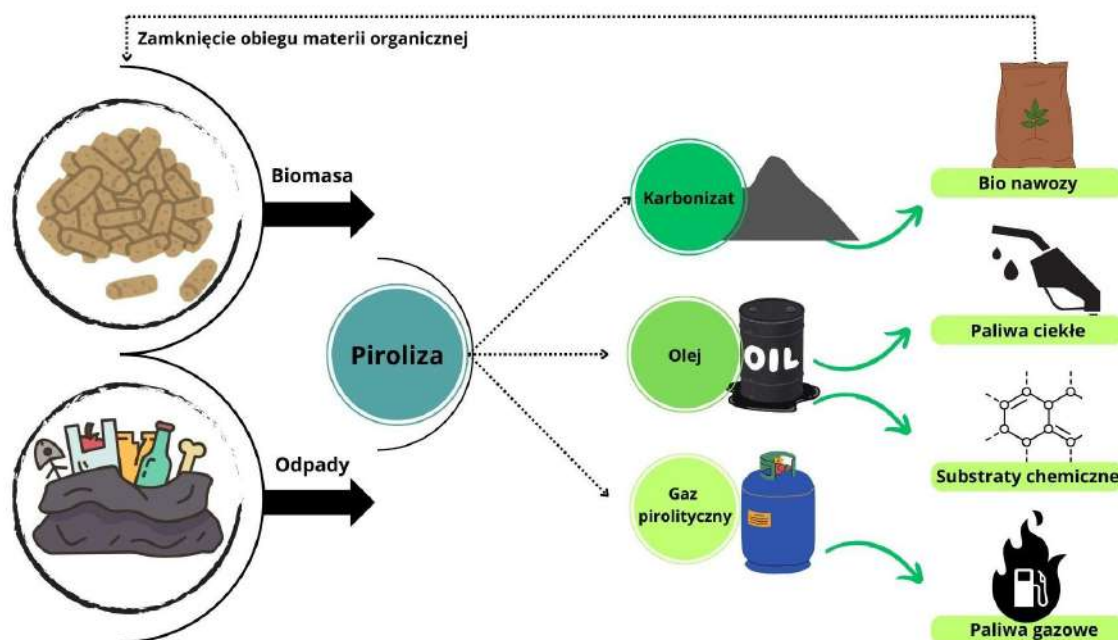


Rys. 2 Porównanie różnych metod termicznego przetwarzania RDF [49–53]

Dane literaturowe wskazują, że spośród wszystkich wymienionych procesów, piroliza jest jedną z najbardziej perspektywicznych, ekonomicznych i efektywnych metod utylizacji odpadów [54,55]. Piroliza jest uważana za proces recyklingu chemicznego i w przeciwieństwie do spalania umożliwia odzysk zarówno energii, jak i stałych (bogatych w węgiel) oraz ciekłych i gazowych produktów węglowodorowych [47]. Proces pirolizy pozwala na odzysk cennych składników z odpadów, co doskonale wpisuje się w ideę gospodarki o obiegu zamkniętym [56]. Ponadto produkty pirolizy można wykorzystać w celach energetycznych i produkcyjnych, a sam proces może ograniczyć

problem składowania odpadów i emisji szkodliwych substancji i gazów cieplarnianych [4,57].

Piroliza prowadzona jest w warunkach inertnych, najczęściej w atmosferze azotu, bez dostępu tlenu i prowadzi do powstawania produktów stałych (karbonizat), ciekłych (olej pirolityczny) i gazowych (gaz pirolityczny) (rys. 3) [58,59]



Rys. 3 Schemat ideowy pirolizy [58,59]

Piroliza ma szereg zalet, które dają jej przewagę nad innymi procesami termicznego przekształcania odpadów [60]. Główną zaletą pirolizy jest jej elastyczność w doborze parametrów, takich jak temperatura, ciśnienie i czas przebywania [61], które decydują o udziale poszczególnych frakcji tego procesu [62]. Ponadto piroliza charakteryzuje się niską emisją tlenku węgla (CO) i dwutlenku węgla (CO₂), co czyni proces bardziej przyjaznym dla środowiska [8]. Inwestycja w instalację do pirolizy zapewnia wysoką stopę zwrotu, co uzasadnia opłacalność jej budowy [63].

Technologia pirolizy charakteryzuje się dużym potencjałem, dzięki któremu w sposób przyjazny dla środowiska można przekształcać różnego rodzaju odpady stałe, w tym biomasę [64,65], tworzywa sztuczne [66,67] i ich mieszaniny [68,69], tworząc wartościowe produkty chemiczne i paliwa [50]. Obecność tworzyw sztucznych w strumieniu odpadów poddawanych pirolizie zwiększa wartość opałową wytworzonych produktów, zmniejsza wytwarzanie tlenu i zmniejsza udział karbonizatu w produktach pirolizy [70,71]. Dodatkowo piroliza wyróżnia się wyższą efektywnością odzysku energii z odpadów w porównaniu do innych metod utylizacji, odzysk energii sięga 80% [72].



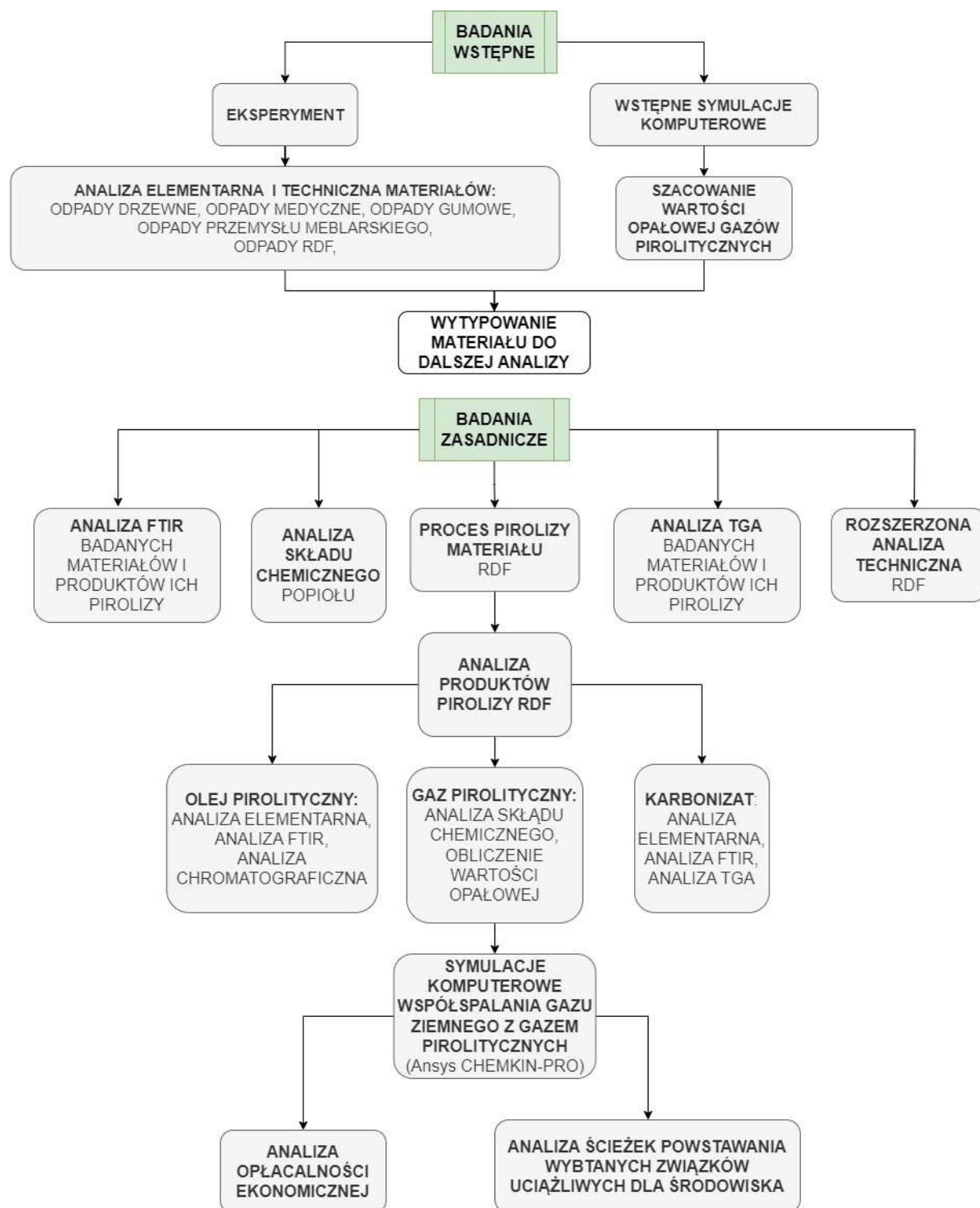
Dotychczasowe metody zagospodarowania gazu pirolitycznego koncentrowały się w dużej mierze na wykorzystaniu całego wyprodukowanego gazu do utrzymania ciągłości pracy instalacji pirolitycznej. Jest to popularne rozwiązanie, które zostało szczegółowo opisane przez Liu i inni [73].

Innym sposobem wykorzystania gazu pirolitycznego jest propozycja jego wykorzystania jako paliwa alternatywnego w silnikach spalinowych [74].

Oprócz gazu pirolitycznego na uwagę zasługuje powstały podczas procesu karbonizat. Materiał ten z powodzeniem może zostać rozważony jako substytut węgla kamiennego, wykorzystywanego podczas produkcji stali.

3. Metodyka badawcza

Zakres badań obejmował badania wstępne, badania zasadnicze, symulacje komputerowe oraz analizę ekonomiczną. Schemat wszystkich przeprowadzonych badań został przedstawiony na rysunku 4.



Rys. 4 Schemat przeprowadzonych badań



Badania laboratoryjne zostały przeprowadzone na Wydziale Inżynierii Materiałowej i Informatyki Przemysłowej (Katedra Techniki Ciepłej i Ochrony Środowiska) Akademii Górniczo-Hutniczej w Krakowie, w ramach stażu naukowego.

Zakres badań obejmował:

- badania wstępne:
 - przygotowanie próbek badanych materiałów (mielenie w młynku kulowym firmy Retsch, w celu uzyskania frakcji poniżej 200 μm),
 - analiza techniczna materiału badawczego:
 - zawartość popiołu,
 - zawartość wilgoci,
 - zawartość części lotnych,
 - analiza elementarna materiału badawczego,
- badania zasadnicze:
 - uzupełnienie analizy technicznej o:
 - szczegółową analizę techniczną,
 - zawartość chloru,
 - skład chemiczny popiołu,
 - proces pirolizy materiałów RDF w celu zebrania powstałych produktów,
 - analiza produktów pirolizy, a mianowicie:
 - analiza frakcji stałej (karbonizat) – analiza elementarna, analiza TGA, analiza FTIR,
 - analiza frakcji ciekłej (kondensat) – analiza elementarna, analiza TGA, analiza FTIR, analiza chromatograficzna,
 - analiza frakcji gazowej – analiza składu chemicznego, obliczenie wartości opałowej,
 - symulacje komputerowe mające na celu oszacowanie składu gazów spalinowych powstałych podczas współspalania gazu ziemnego z gazami pirolitycznymi (Ansys Chemkin PRO v. 2021 R1),
 - analiza ekonomiczna opłacalności implementacji reaktora do pirolizy ciągłej w istniejącym ciągu technologicznym huty stali,
 - analiza ścieżek powstawania wybranych związków uciążliwych dla środowiska.

Do badań wstępnych wytypowano następujące materiały:

- drewno sosnowe w postaci zrębków o wymiarach ok. 2-3 cm (rys. 5a),

- drewno olchowe w postaci zrębków o wymiarach ok. 3-4 cm (rys. 5b),
- odpady medyczne (maseczka ochronna) (rys. 5c),
- odpady gumowe (rozdrobnione części opon samochodów osobowych w postaci granulatu o wymiarach ok. 3-5 mm) (rys. 5d),
- odpady z przemysłu meblarskiego (płyty MDF w formie pelletu, który miał średnie wymiary 0,5-2 cm długości i średnicę 0,8 cm. Materiał był twardy i jednorodny) (rys. 5e),
- odpady RDF (w formie pelletu, który miał średnie wymiary 0,5-1 cm długości i 0,5 cm średnicy. Materiał był kruchy i niejednorodny) (rys. 5f).

Następnie dla celów analizy technicznej i elementarnej materiał został rozdrobniony za pomocą młynka kulowego Retsch i przesiany w celu uzyskania frakcji 200 μm .



a)



b)



c)



d)



e)



f)

Rys. 5. Materiały użyte do badań: a) zrębki sosnowe, b) zrębki olchowe, c) maseczka ochronna, d) odpady gumowe z opon, e) pellet MDF, f) pellet RDF.

Do badań wykorzystano aparaturę przedstawioną w tabeli 1.

Tabela 1. Aparatura badawcza zastosowana w badaniach

Rodzaj aparatury	Nazwa	Parametry
Analizator CHN	Leco Truspec CHN628	Możliwość identyfikacji następujących składników: C, H, N.
Chromatograf gazowy	Agilent Technology 7890A GC	Możliwość identyfikacji następujących składników: H ₂ , CH ₄ , CO ₂ , CO, O ₂ , N ₂ , C _x H _y (C ₂ H ₆ , C ₂ H ₄ , C ₂ H ₂)
Spektrometr FTIR	Bruker Alpha II, z jednostką ATR oraz detektorem DLaTGS	Zakres liczby falowej 4000-400 cm ⁻¹ , rozdzielczość 4cm ⁻¹
Waga precyzyjna	PR223 OHAUS PRseries	Maksymalny zakres ważenia 220 g, rozdzielczość 0,001 g
Analizator termograwimetryczny	Mettler Toledo TGA/DSC 3+	Zakres temperatury od – 150 do 1600°C

3.1. Analiza techniczna i elementarna

Analiza techniczna została wykonana zgodnie z poniższymi normami:

- oznaczenie zawartości popiołu została wykonane według normy EN 15403:2011 NP.,
- oznaczenie zawartości wilgoci została wykonane według normy EN 15414-3:2011 NP.,
- oznaczenie zawartości części lotnych została wykonane według normy EN 15402:2011 NP.,
- oznaczenie ciepła spalania zostało wykonane według normy PN-EN 15400:2011,
- oznaczenie składu chemicznego popiołu zostało wykonane zgodnie z Q/LP/65/B:2016,
- oznaczenie zawartości chloru został wykonane zgodnie z Q/LP/24/B:2016,
- oznaczenie zawartości rtęci został wykonane zgodnie z Q/LP/54/B:2016.

Analizę elementarną wykonano w celu oznaczenia zawartości węgla NP., wodoru (H) i azotu (N). Analizę wykonano przy użyciu analizatora Leco Truspec CHN628 LECO. Działanie analizatora opiera się na metodzie wysokotemperaturowego (950°C) spalania w tlenie, nazywanej inaczej metodą Dumasa. Zapewnia ona szybkie, zupełne i całkowite spalenie próbki, a konkretne udziały poszczególnych pierwiastków określone są za pomocą detektorów absorpcji w podczerwieni (C i H) bądź detektora termoprzewodnościowego (N).

Uzyskane wyniki przedstawiono w tabeli 2.

Tabela 2. Wyniki analizy technicznej i elementarnej badanych materiałów

Parametr	Zrębki sosnowe	Zrębki olchowe	Maseczka ochronna	Granulat z opon	MDF	RDF	NP.
Analiza techniczna							
Zawartość wilgoci ^a [%]	3,1	4,5	1,2	2,0	5,5	3,8	0,1
Zawartość popiołu ^a [%]	1,6	1,3	4,8	4,2	1	20,7	0,2
Zawartość części lotnych ^a [%]	81,5	87,6	95,2	62,8	76,4	64,9	0,5
Ciepło spalania [MJ/kg]	20,2	19,6	-	35,4	-	24,3	0,2
Analiza elementarna							
Zawartość C ^a [%]	49,5	47,5	76,4	79,8	46,8	52,4	0,6
Zawartość H ^a [%]	6,4	6,4	11,7	6,7	6,2	6,7	0,3
Zawartość N ^a [%]	0,07	0,3	1,1	0,3	3,6	0,7	0,01
Zawartość S ^a [%]	0,06	0,2	0,2	1,5	-	0,2	0,01
Zawartość O ^a [%]	43	40,9	4,7	6,5	-	33,2	0,8

^a – stan analityczny (próbki wysuszone w 105°C i zmielone poniżej 1 mm),

NP. – niepewność pomiarowa

Na podstawie badań analizy elementarnej oszacowano i obliczono wartość opałową gazów pirolitycznych, powstałych po pirolizie badanych materiałów. Symulacji dokonano z wykorzystaniem programu Chemkin v. 2021. Dla materiału MDF i RDF wartość opałowa została obliczona na podstawie tablic Raznjevicia [75]. Uzyskane wyniki zamieszczono w tabeli 3.

Tabela 3. Zestawienie obliczonej wartości opałowej gazów pirolitycznych

Gaz pirolityczny z odpadów	Jednostka	Wartość opałowa	NP.	Źródło
Zrębek olchowych	[MJ/m ³]	16,2	0,40	Symulacje komputerowe opublikowane w pracy [76]
Zrębek sosnowych		12,9		Symulacje komputerowe opublikowane w pracy [76]
Maseczek ochronnych		47,7		Symulacje komputerowe opublikowane w pracy [77]
Granulatu z opon		<40		Badania własne
Odpadu MDF		13,03-16,03		Badania własne
Odpadu RDF		14,3 – 20,5		Badania własne

Biorąc pod uwagę uwarunkowania technologiczne wybranego pieca przepychowego oraz fakt, że palniki i układ spalania są przystosowane do spalania gazu o maksymalnej wartości opałowej nieprzekraczającej 35 MJ/m³, do dalszego etapu badań wybrano tylko jeden z badanych pierwotnie materiałów, a mianowicie odpady RDF. Biorąc pod uwagę uzyskane wartości opałowe testowanych gazów oraz problem

z zagospodarowaniem gorszych jakościowo klas RDF-u oraz jego zaleganiem na składowiskach, poddanie termicznemu przekształceniu ww. odpadów wydaje się ekonomicznie opłacalne oraz korzystne dla środowiska naturalnego.

W następnym etapie, tj. podczas przeprowadzania badań zasadniczych, poszerzono analizę techniczną o obliczenie zawartości rtęci oraz chloru. Kompleksowa analiza techniczna i elementarna dla odpadu RDF została zamieszczona w tabeli 4.

Tabela 4. Kompleksowa analiza techniczna i elementarna dla odpadu RDF

Parametr	Jednostka	Wartość	NP.
Analiza techniczna			
Zawartość wilgoci całkowitej	[%]	2,7	0,3
Zawartość wilgoci w stanie analitycznym		3,4	0,2
Zawartość popiołu w stanie analitycznym		17,9	0,8
Zawartość popiołu w stanie roboczym		17,6	0,8
Zawartość popiołu w stanie suchym		18,1	0,8
Zawartość części lotnych w stanie analitycznym		72,9	0,6
Zawartość części lotnych w stanie suchym		75,0	0,7
Zawartość części lotnych w stanie suchym i bezpopiołowym		91,6	0,9
Zawartość chloru w stanie analitycznym		0,76	0,16
Zawartość rtęci w stanie suchym	[mg/kg]	0,19	0,03
Ciepło spalania w stanie analitycznym	[MJ/kg]	24,3	-
Ciepło spalania w stanie suchym		25,2	-
Ciepło spalania w stanie roboczym		22,8	-
Analiza elementarna			
Zawartość C ^a	[% mas.]	52,4	0,6
Zawartość H ^a		6,7	0,3
Zawartość N ^a		0,7	0,01
Zawartość S ^a		0,2	0,01
Zawartość O ^a		33,2	0,8
Zawartość Cl ^a		0,8	0,6

^a – w stanie analitycznym,

* do przeliczenia zawartości wykorzystano wynik zawartości wilgoci analitycznej 3,4%.

Analiza techniczna dla wybranego materiału wykazała niską zawartość wilgoci całkowitej. Dla RDF-u wynosiła ona 2,7%. Zawartość popiołu w badanym materiale okazała się wysoka, bo wynosiła ponad 18%. Jest to spowodowane tym, że RDF w swoim składzie zawiera różne materiały pochodzące z nadsitowej frakcji odpadów, w tym plastik, gumę, odpady tekstylne i celulozę. Zawartość substancji lotnych wynosiła dla RDF-u 75%, zaś ciepło spalania w stanie suchym wynosiła 25,2 MJ/kg. Analiza elementarna wykazała wysoką, ponad 50% zawartość węgla i stosunkowo wysoką zawartość wodoru (6,7%).

Analizę techniczną uzupełniono o badanie składu chemicznego otrzymanego popiołu. Uzyskane wyniki zamieszczono w tabeli 5.

Tabela 5. Wyniki analiz składu chemicznego popiołu uzyskanego z RDF

Parametr	Jednostka	Wartość	NP
Zawartość SiO ₂	[%]	33,6	1,4
Zawartość Al ₂ O ₃		15,9	1,6
Zawartość Fe ₂ O ₃		6,3	0,7
Zawartość CaO		23,1*	-
Zawartość MgO		1,7	0,05
Zawartość P ₄ O ₁₀ (P ₂ O ₅)		1,1	0,02
Zawartość SO ₃		2,2	0,08
Zawartość Mn ₃ O ₄		0,13	0,01
Zawartość TiO ₂		3*	-
Zawartość BaO		0,1	0,01
Zawartość SrO		0,06	0,01
Zawartość Na ₂ O		2,8	0,3
Zawartość K ₂ O		1,8	0,2

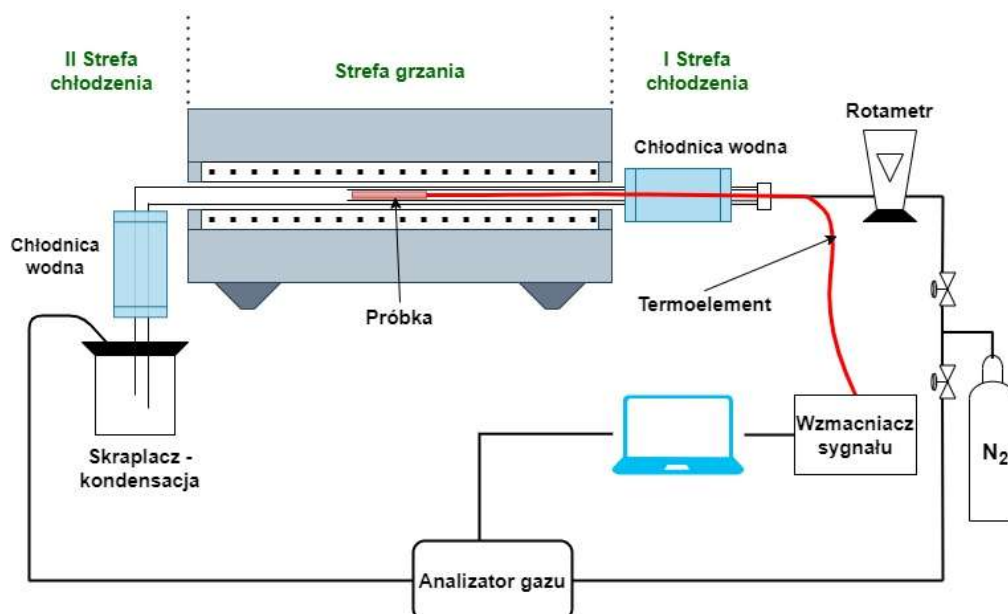
* Wynik poza zakresem akredytacji

W składzie popiołu dominowały tlenki SiO₂, Al₂O₃, Fe₂O₃ oraz CaO (którego stężenie przekroczyło zakres akredytacji użytego sprzętu). Dominacja ww. tlenków charakteryzuje zazwyczaj popioły węglowe. Analiza wykazała obecność siarki, potasu i sodu, pierwiastków odpowiedzialnych za korozję [78]. Dominująca zawartość SiO₂ jest charakterystyczna dla popiołów pochodzących ze spalania odpadów RDF [79].

3.2. Piroliza RDF

Proces pirolizy analizowanych odpadów RDF (w postaci pelletu) przeprowadzono na stanowisku badawczym przedstawionym na rysunku 6. Stanowisko badawcze zbudowane było z trzech stref, a mianowicie: I strefa chłodzenia, strefa grzania i II strefa chłodzenia. W I strefie chłodzenia dostarczany był gaz inertyzujący (N₂) oraz chłodzony był materiał poddawany pirolizie po zakończeniu procesu. Następnie w strefie grzania umieszczane były próbki i prowadzony był proces pirolizy. Powstałe produkty przepływały wzdłuż poziomej rury reaktora, aby dotrzeć do II strefy chłodzenia, gdzie powstałe gazy wraz z nieskondensowaną frakcją ciekłą, były chłodzone dwuetapowo. W pierwszej kolejności gazy ochładzane były do temperatury 18°C w kąpeli wodnej, następnie w pojemniku z lodem do 4°C. Dzięki temu uzyskiwano frakcję ciekłą bogatą m.in. w węglowodory, a gaz pirolityczny kierowany był bezpośrednio do gromadzenia w worku próbobiornym typu Tedlar®, w celu przeprowadzenia chromatografii gazowej.

Pirolizę prowadzono dla dwóch temperatur 600°C i 800°C. Czas wytrzymania próbki wynosił 3 i 6 min. Czas nagrzania próbki do temperatury procesu wynosił 4 min. Strumień podawanego azotu był na poziomie 0,2 dm³/min. Uzyskany gaz został zebrany do worka próbobiornego i poddany chromatografii gazowej.



Rys. 6. Schemat stanowiska do pirolizy

Po przeprowadzeniu procesu pirolizy określono uzysk otrzymanych produktów (tabela 6).

Tabela 6. Uzysk poszczególnych produktów w procesie pirolizy

	Karbonizat	Olej pirolityczny	Gaz pirolityczny
Jednostka	[%]		
Piroliza RDF_600/3	43,03	44,4	21,6
Piroliza RDF_600/6	36,7	27,3	36
Piroliza RDF_800/3	29,4	24,3	46,3

W przypadku RDF-u zarówno wzrost czasu przetrzymania próbki, jak i wzrost temperatury procesu miały pozytywny wpływ na wzrost uzysku frakcji gazowej. Zwiększenie temperatury procesu z 600 do 800°C przyczyniło się do ponad dwukrotnego wzrostu uzysku gazu z 21,6% do 46,3%. Na zmniejszenie uzysku oleju pirolitycznego miały wpływ zarówno wzrost temperatury procesu, jak i wydłużony czas wytrzymania próbki. Uzysk karbonizatu zmniejszał się również wraz ze wzrostem temperatury procesu i wydłużeniem czasu wytrzymania próbki.

W obu przypadkach wzrost temperatury procesu miał znaczący wpływ na zwiększenie uzysku frakcji gazowej.

Poddane dalszej analizie produkty pirolizy uzyskano dla następujących wariantów prowadzenia procesu:

- odpad RDF, temperatura procesu 600°C, czas wytrzymania próbki 3 min. – RDF_600/3,

- odpad RDF, temperatura procesu 600°C, czas wytrzymania próbki 6 min. – RDF_600/6,
- odpad RDF, temperatura procesu 800°C, czas wytrzymania próbki 3 min. – RDF_800/3.



a)

b)

c)

Rys. 7. Produkty pirolizy: a) gaz pirolityczny przechodzący przez osuszacz, b) kondensat, c) karbonizat.

3.2.1. Gaz pirolityczny

Otrzymany w procesie pirolizy gaz został poddany analizie chromatograficznej. Uzyskane wyniki chromatografii gazowej zamieszczono w tabeli 7.

Tabela 7. Skład chemiczny gazu uzyskany dla różnych wariantów prowadzenia procesu.

Gaz	Jednostka	RDF_600/3	RDF_600/6	RDF_800/3
H ₂	(%)	16	12,5	12
CO ₂		20,7	16,5	17,4
CO		24,7	42,2	31,7
CH ₄		33,9	23,9	25,4
C ₂ H ₂		-	0,2	-
C ₂ H ₄		1,6	3	10,5
C ₂ H ₆		3	1,5	2,8
C ₄ H ₈		-	-	0,09
Wartość opałowa		19,9	18,1	22,5

W przypadku pirolizy RDF-u skład gazu różnił się, ze względu na dużą niejednorodność badanego materiału. Można zauważyć, że wydłużony czas przetrzymania próbki wpłynął negatywnie na uzysk metanu (z 33,9 na 23,9%)

w uzyskanym gazie. Na zmniejszenie udziału węglowodorów miało wpływ wydłużenie czasu przetrzymania próbki. Wyższa temperatura pirolizy nie wpłynęła na zwiększenie udziału węglowodorów. Dla RDF-u, który był mocno niejednorodny, na wartość opałową nie miał znaczącego wpływu wydłużony czas wytrzymania próbki. Dopiero zwiększenie temperatury procesu wpłynęło pozytywnie na zwiększenie wartości opałowej do ponad 20 MJ/m³, co było spowodowane wzrostem udziału węglowodorów w składzie uzyskanego gazu.

3.2.2. Olej pirolityczny (kondensat)

Zebrany olej pirolityczny (rys. 8b) został poddany analizie elementarnej, FTIR oraz chromatografii gazowej sprzężonej ze spektrometrią mas.

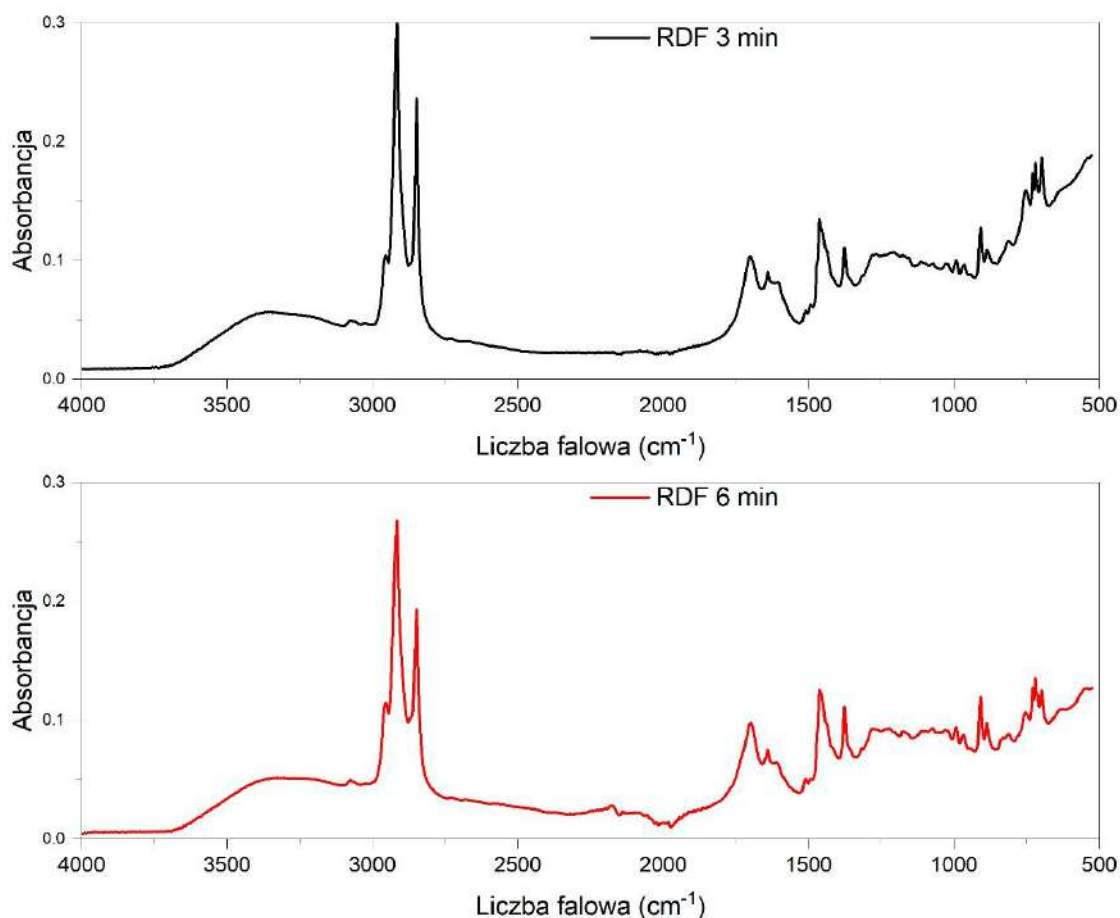
W tabeli 8 przedstawiono skład elementarny kondensatów uzyskanych w wyniku pirolizy.

Tabela 8. Skład elementarny i ciepło spalania kondensatów

	C		H		N		O		LHV
	[% mas.]	NP	[% mas.]	NP	[% mas.]	NP	[% mas.]	NP	[MJ/kg]
Kondensat RDF 600/3	60,6	1,3	9,3	0,3	1,2	0,1	16,3	0,3	30,4
Kondensat RDF 600/6	69,5	1	10,3	0,4	1,4	0,3	16	0,6	34,7

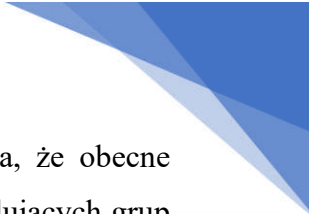
Udział C, H, N, O mieścił się w zakresie wartości dla próbek olejów popirolitycznych. Zawartość poszczególnych pierwiastków w tym przypadku jest mocno uzależniona od składu elementarnego w przetwarzanych surowcach (lub proporcji między nimi w przypadku mieszanin takich jak RDF). Większy udział tworzyw sztucznych może wpływać na podwyższenie udziału pierwiastka C i H w kondensacie. Skład elementarny został wykorzystany do oszacowania wartości ciepła spalania z wykorzystaniem popularnych w literaturze wzorów empirycznych. Przykładowo, wartość ciepła spalania w tym wypadku wynosiła 30,4 MJ/kg oraz 34,7 MJ/kg odpowiednio dla próbek kondensatu RDF_600/3 oraz RDF_600/6 w przypadku przeliczenia według zależności Boie [80]. Różnicę bilansową pierwiastków elementarnych pomiędzy masą jednostkową, a sumarycznym udziałem poszczególnych pierwiastków może stanowić materia mineralna (szczególnie pochodząca z cząstek stałych uciekających z układu reakcyjnego) lub zawartości chloru.

Następnie wykonano analizę FTIR-ART. Na rysunku 8 przedstawiono widma zarejestrowane techniką osłabionego odbicia (ATR) w zakresie podczerwieni dla testowanych dwóch próbek kondensatów.



Rys. 8. Widma FTIR-ATR analizowanych próbek kondensatów popirolitycznych

Testowane próbki stanowią heterogeniczne mieszaniny wykazujące pasma absorpcji charakterystyczne dla licznych grup funkcyjnych. Wśród zidentyfikowanych pasm szczególnie intensywne są pasma grup alifatycznych w zakresie liczby falowej 2950-2800 cm^{-1} odpowiadające drganiom połączeń CH. Wśród nich najwyraźniejsze są pasma odpowiadające drganiom asymetrycznym rozciągającym grup CH_2 (2920 cm^{-1}) oraz drganiom rozciągającym symetrycznym grup CH_2 (2850 cm^{-1}). Obecne, choć z mniejszą intensywnością są w tym zakresie pasma absorpcyjne dla grup metylowych (np. 2950 cm^{-1}). Potwierdzeniem obecności związków alifatycznych, szczególnie metylenowych, są również widoczne pasma drgań nożycowych CH_2 w zakresie liczby falowej 1460-1440 cm^{-1} . Warto zaznaczyć, że pasma te mogą pokrywać się również z drganiami asymetrycznymi deformacyjnymi grup CH_3 . Ponadto potwierdzeniem wniosków są również widoczne pasma dla drgań kołyszących $-(\text{CH}_2)_n-$ w zakresie 740-

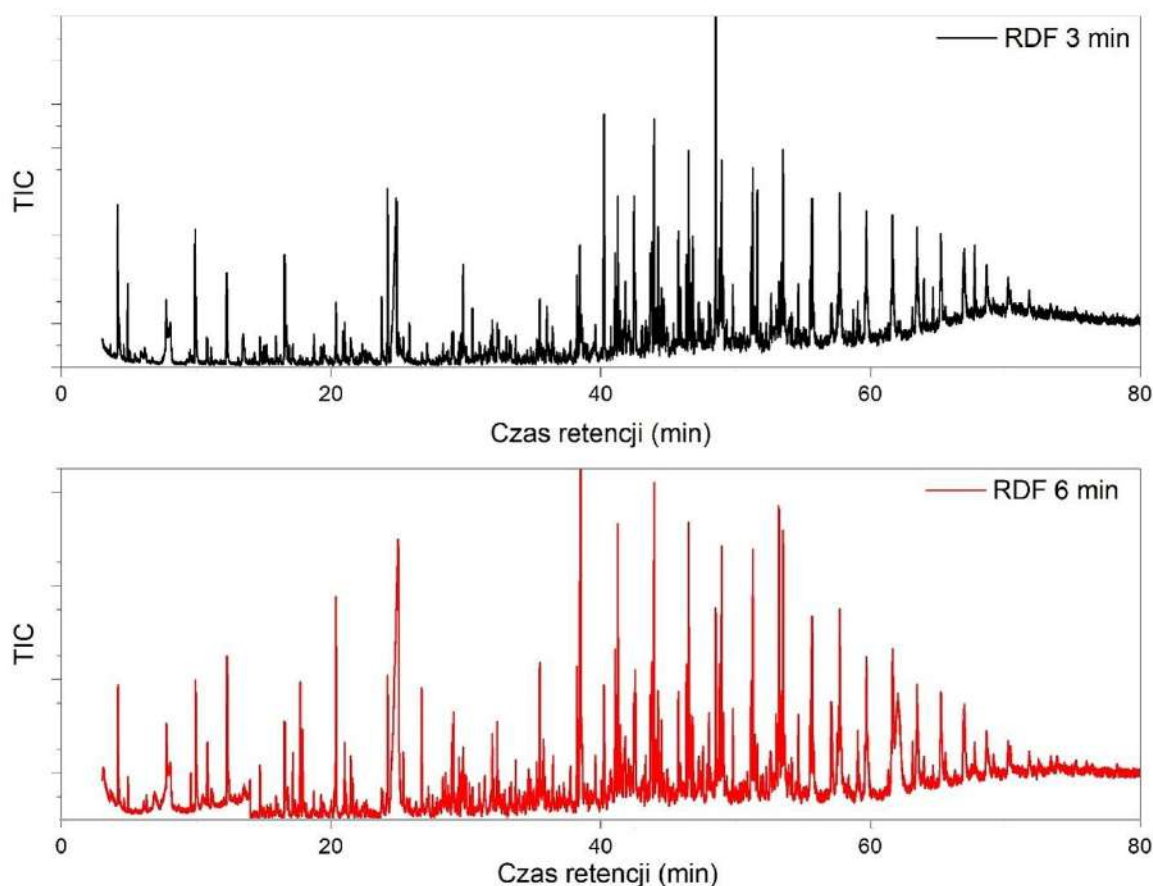


720 cm^{-1} . Pasma to rozdziela się, co stanowi podstawę do stwierdzenia, że obecne w testowanym kondensacie struktury mogą zawierać ponad dziesięć sąsiadujących grup czyli stanowić molekuly alifatyczne o większych zakresach mas cząsteczkowych. Wśród wspomnianych związków alifatycznych obecne są terminalne olefiny, o czym świadczy obecność pasma absorpcyjnego w zakresie 3080 cm^{-1} , które można przypisać grupie winylowej ($-\text{CH}_2=\text{CH}_2$). Może to być rezultat rozkładu poliolefin oraz polimerów winylowych. Na widmie obu analizowanych próbek można jednocześnie zaobserwować pasma w 1640 i 1600 cm^{-1} , co świadczy, że wspomniane ugrupowania mogą być odpowiednio z niczym nie skoniungowane lub skoniungowane z grupami $\text{C}=\text{O}$ oraz $\text{C}=\text{C}$. Analizując zarejestrowane widma, warto również zauważyć obecność pasm charakterystycznych dla tlenowych grup funkcyjnych. W zakresie liczby falowej 3500-3200 cm^{-1} widoczne jest pasmo dla drgań rozciągających O-H oraz pasmo drgań rozciągających dla grupy karbonylowej w 1700-1650 cm^{-1} . Występowanie tych pasm może świadczyć o obecności kwasów karboksylowych albo pochodnych im estrów. Występowanie wspomnianego szerokiego pasma w zakresie 3500-3200 cm^{-1} może również świadczyć o niewielkiej obecności alkoholi pierwszo- oraz drugorzędowych. Dowodzić tego może pasmo o niewielkiej intensywności w zakresie 1100-1050 cm^{-1} charakterystyczne dla drgań rozciągających $-\text{C}-\text{O}$.

Charakter widm analizowanych próbek kondensatów popirolitycznych, dla których obserwuje się bardzo zbliżone położenie i kształt pasm absorpcji świadczy o ich bardzo zbliżonym składzie jakościowym. Warto jednak zauważyć, że obecne są pewne relatywne różnice pomiędzy poszczególnymi pasmami, co może świadczyć z kolei o pewnych różnicach ilościowych w ich składzie.

W następnym etapie próbki kondensatu poddano chromatografii gazowej sprzężonej ze spektrometrią mas.

Na rysunku 9 przedstawiono chromatogramy kondensatów uzyskanych w różnych warunkach procesowych.



Rys. 9. Chromatogramy analizowanych próbek kondensatów popirolitycznych

Jak można zauważyć, kondensaty stanowią wysoce złożone mieszaniny, które zawierają liczne związki organiczne. W wyniku całkowania uzyskanych chromatogramów wykryto ponad 200 pików/związków. Do dalszej analizy poddawano piki, które stanowiły nie mniej niż 2% najwyższego pików. Identyfikacja związków polegała na porównaniu uzyskanych dla nich widm z danymi zawartymi w bibliotece MS (NIST14). W załączniku 1 zebrano wybrane związki (78 związków), których stopień dopasowania stanowił nie mniej niż 60% dopasowania według stosowanej procedury identyfikacji. Uzyski są przedstawione jako udziały relatywne obliczane jako powierzchnia poszczególnego pików do sumy powierzchni pików, które zostały całkowane.

Należy zauważyć, iż analiza składu techniką FTIR wydaje się pozostawać w pełnej zgodności z wynikami analiz próbek łączonymi technikami GC-MS. Wśród zidentyfikowanych związków warto zauważyć wysoki udział węglowodorów alifatycznych. Potwierdzając analizę FTIR warto szczególnie podkreślić obecność terminalnych olefin. Obecne są również terminalne dieny potwierdzające łącznie obecność dominującej zawartości poliolefin w badanym RDFie. Potwierdza to również

kształt charakterystycznego „grzebienia” widoczny w drugiej części chromatogramu (kolor czarny) – typowy dla rozkładu poliolefin, gdzie obserwuje się kolejno dieny, olefiny i alkeny o stopniowo rosnącej liczbie atomów węgla w cząsteczkach. Wśród nich zidentyfikowano węglowodory od C10 do C26. Wykryto również występowanie różnego rodzaju związków o charakterze aromatycznym. Mogą one być efektem przetwarzania źródłowej materii w wysokich temperaturach lub obecności w przetwarzanej materii struktur polimerowych takich jak np. polistyren. Obecność związków tlenowych w kondensacie (np. cyklicznych ketonów lub związków furanowych) może dowodzić obecności pewnych odpadowych struktur biomasowych w testowanej mieszaninie. W produktach zidentyfikowano również pewne chlorowcopochodne, które mogą świadczyć o obecności np. PCV w surowcu lub dodatków na polimerów opartych na związkach chlorowcopochodnych.

3.2.3. Karbonizat

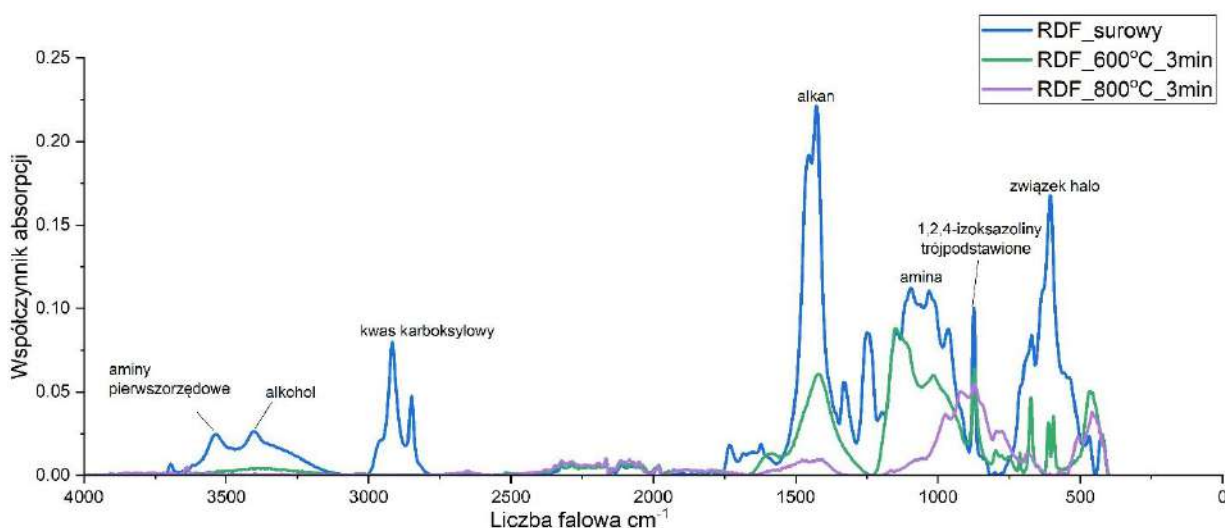
Uzyskany podczas badania karbonizat (rys. 8c) również został poddany analizie elementarnej. Uzyskane wyniki zostały przedstawione w tabeli 9.

Tabela 9. Analiza elementarna uzyskanego karbonizatu

Nazwa próbki	N	C	H
Jednostka	[%]		
RDF karbonizat 600/3	0,9	36,7	1,3
RDF karbonizat 600/6	0,9	34,7	1,1

W przypadku RDFu zawartość węgla jest niższa w karbonizatach w porównaniu do materiału surowego. Dłuższy czas wytrzymania próbki podczas procesu pirolizy, również miał wpływ na obniżenie zawartości węgla w karbonizacie. Dla zawartości azotu odnotowano jedynie minimalne zmiany wartości. Dla zawartości wodoru również zaobserwowano spadek w karbonizatach, w porównaniu do materiału surowego.

Otrzymany karbonizat poddano analizie FTIR, a wyniki porównano z surowym RDFem. Uzyskane wyniki przedstawiono na rysunku 10.



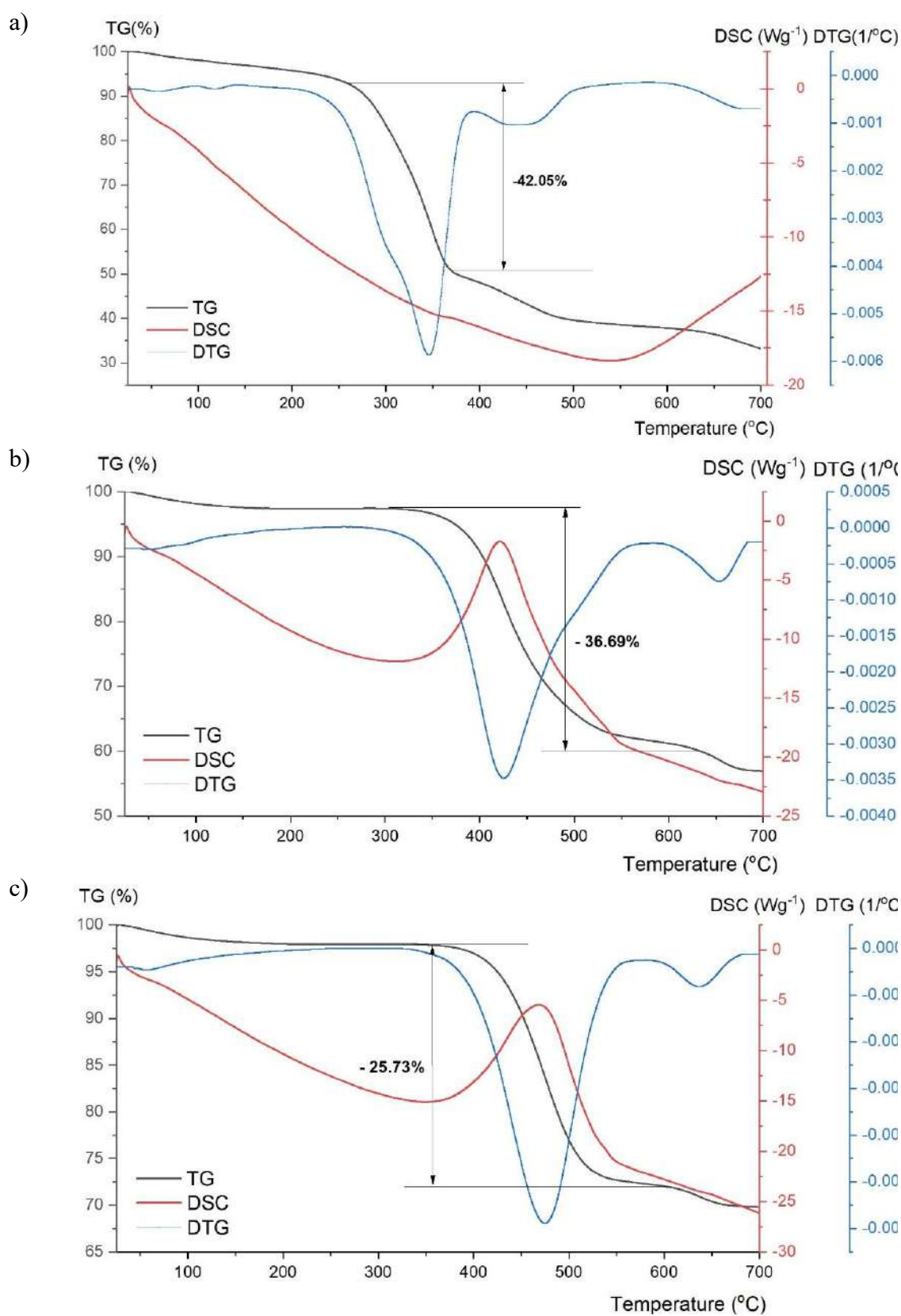
Rys. 10 Krzywe FTIR dla badanego odpadu RDF.

W surowym RDF (rys.10) można zaobserwować występowanie drgań rozciągających odpowiadających za obecność wiązań O-H (alkohole, fenole: 3700-3500 cm^{-1}), dodatkowo występują drgania rozciągające odpowiadające za wiązania O-H (kwasy karboksylowe: 2500-330 cm^{-1}), obecne są drgania rozciągające C-H (węglowodory alifatyczne: 3000-2850 cm^{-1}) oraz drgania rozciągające odpowiadające za wiązania deformacyjne O-H (1450-1200 cm^{-1}).

W karbonizacji z pirolizy w temperaturze 600°C występują drgania rozciągające odpowiadające za wiązania O-H (kwasy karboksylowe: 2500-330 cm^{-1}), występują także drgania rozciągające odpowiadające za wiązania C=C (węglowodory aromatyczne: 1610-1500 cm^{-1}) i drgania deformacyjne O-H (1450-1200 cm^{-1}).

W karbonizacji z pirolizy w temperaturze 800°C nie odnotowano wyraźnych pików w zakresie od 4000 do 1260 cm^{-1} , co wskazuje że większość związków i wiązań w tym zakresie została zdegradowana podczas procesu pirolizy [81,82].

Uzyskany w procesie pirolizy karbonizat poddano analizie TGA wraz z jej pochodnymi DTG i DSC. Uzyskane wyniki przedstawiono na rysunku 11.



Rys. 11 Wykresy TG-DSC gdzie: a) surowy RDF, b) RDF 600/3, c) RDF 800/3



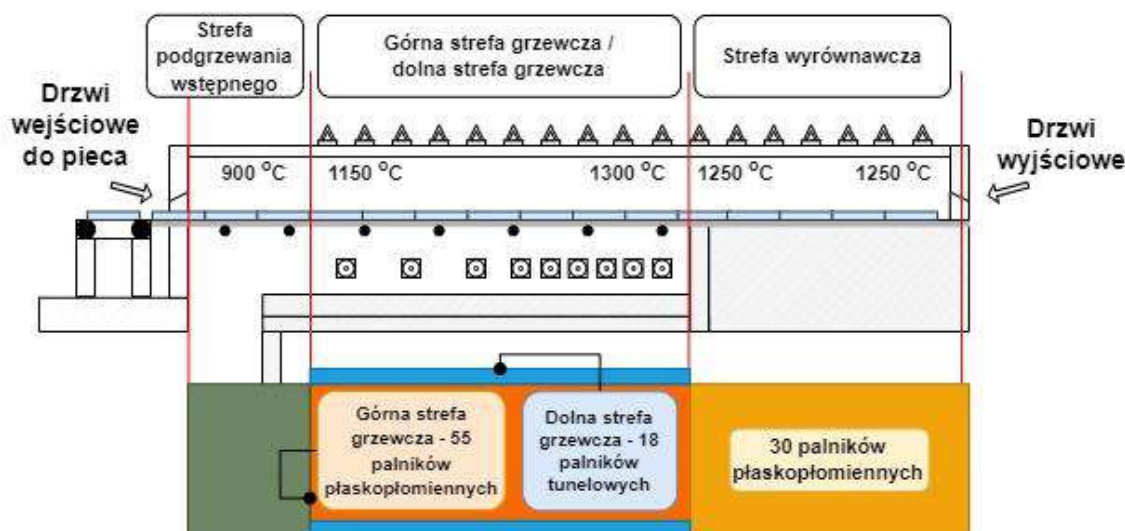
Surowy RDF (rys. 11a) poddany analizie TGA prowadzonej do temperatury 700°C i w atmosferze N₂, odnotował największy ubytek masy w zakresie temperatur 260-370°C (42,05%) z maksymalnym pikiem DTG przy 342°C, etap ten związany jest głównie z degradacją elementów z tworzyw sztucznych, a także elementów celulozowych. Kolejny ubytek masy odnotowano w temperaturze 370-480°C (10%). Drugi, mniejszy pik dla DTG zaobserwowano w temperaturze 437°C, który można przypisać rozkładowi bardziej stabilnych termicznie składników tworzyw sztucznych (LDPE) lub ligniny [83]. Powyżej temperatury 480°C ubytek masy wynosił 7%.

Karbonizat z procesu pirolizy (rys. 11b) w temperaturze 600°C i czasie przetrzymania próbki 3 min został poddany procesowi spalania w atmosferze powietrza. Największy ubytek masy odnotowano w temperaturze 300-630°C (36,69%) z maksymalnym pikiem DTG przy 423°C, który można przypisać uwolnieniu substancji lotnych i reakcji w fazie gazowej pomiędzy substancją lotną a tlenem [84]. Powyżej temperatury 630°C masa karbonizatu spadła o 4%, co można przypisać spalaniu pozostałości węgla i rozkładowi materii nieorganicznej (pik dla DTG w temperaturze 650°C).

Karbonizat uzyskany z procesu pirolizy (rys. 11c) prowadzonej w temperaturze 800°C i czasie przetrzymania próbki 3 min został również poddany procesowi spalania w atmosferze powietrza. Największy ubytek masy odnotowano w zakresie temperatur 380-610°C (25,73%), z maksymalnym pikiem DTG przy 471°C, który można przypisać uwolnieniu substancji lotnych i reakcji w fazie gazowej pomiędzy substancją lotną a tlenem [84]. Powyżej temperatury 610°C masa karbonizatu zmniejszyła się jedynie o 2%, co wiąże się ze spalaniem pozostałości węgla i rozkładowi materii nieorganicznej (pik dla DTG w temperaturze 634°C) [84].

3.3. Energetyczne wykorzystanie produktów termicznego przekształcenia frakcji nadsitowej odpadów komunalnych

W niniejszej pracy zaproponowano koncepcję współspalania gazu ziemnego z gazem pirolitycznym w piecu hutniczym typu przepychowego, przystosowanym do spalania gazu koksowniczego, pracującego w walcowni blach w jednej z hut stali w Polsce. Wydajność projektowa pieca wynosiła 90 t/h, a moc zainstalowana pieca 72,3 MW. Na rysunku 12 przedstawiono uproszczony schemat pieca przepychowego.



Rys. 12. Uproszczony schemat pieca przepychowego, trójstrefowego [4]

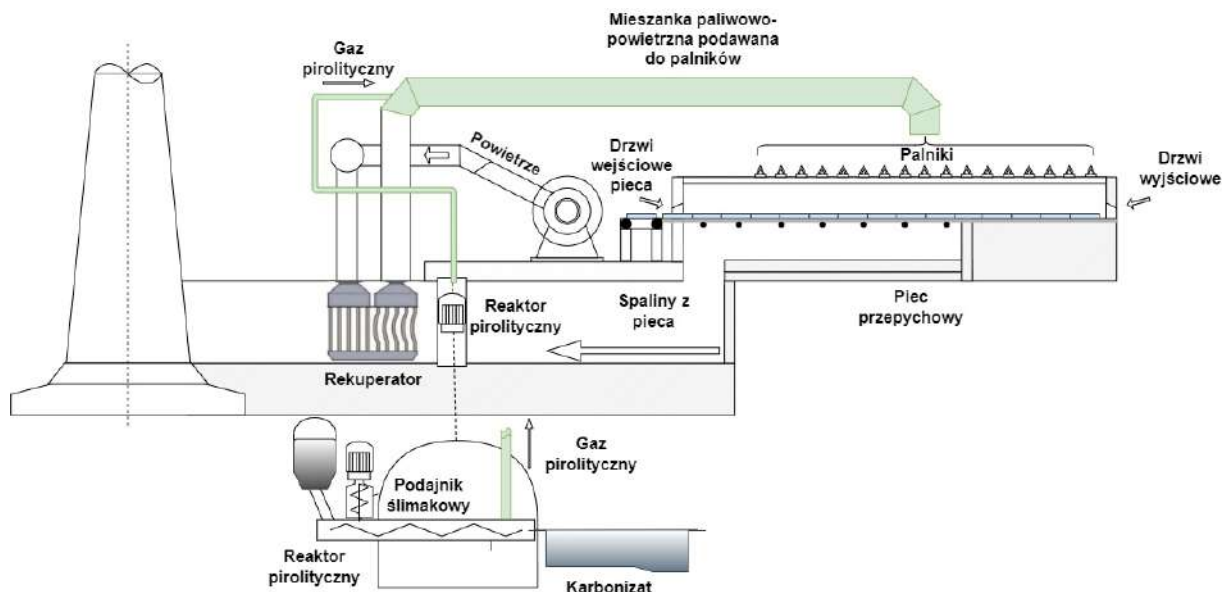
Piec grzewczy typu przepychowego podzielony jest na trzy strefy grzewcze, a mianowicie: strefę podgrzewania wstępnego (900°C), strefę grzewczą (1150÷1300°C), strefę wyrównawczą (1250°C).

Piec jest zaprojektowany do spalania gazu ziemnego lub jego mieszanki z gazem koksowniczym. Pod względem automatyki piec podzielony jest na sześć stref regulacyjnych, wyposażonych w 105 palników zamontowanych na ścianach bocznych i suficie. W proponowanym rozwiązaniu (rys. 13) przyjęto, że huta jest wyposażona w reaktor do pirolizy o wydajności około 1000 kg/h do przetwarzania odpadów lub materiałów pochodzenia biomasowego o maksymalnej wilgotności 10% masowych. Temperatura procesu powinna wahać się w granicach 800°C-900°C, aby uzyskać potrzebną ilość gazu pirolitycznego (50% masy wejściowej). Proces ma na celu produkcję biowęgla, a powstały gaz pirolityczny jest traktowany jako gaz odpadowy, częściowo wykorzystywany do ogrzewania reaktora.

Reaktor o wydajności 1000 kg/h i zdolności przetwórczej 6564 godziny rocznie ma kosztować około 5 300 000 EUR (CAPEX). W zależności od rodzaju odpadów i kaloryczności produktów pochodzących z materiału wejściowego, gaz pirolityczny może stanowić ponad 50% masy wejściowej.

Koncepcja polega na umieszczeniu reaktora pirolizy przed rekuperatorem, co pozwala spalinom opuszczającym piec grzewczy osiągnąć wystarczająco wysoką temperaturę (około 900°C), aby ogrzać reaktor do wymaganego poziomu. Ponadto ciepło ze spalin jest wykorzystywane do wstępnego suszenia i podgrzewania materiału przeznaczonego do procesu pirolizy. Frakcja gazowa wytwarzana w trakcie procesu (bez

chłodzenia lub kondensacji) jest następnie kierowana bezpośrednio do głównego rurociągu, a następnie do palników. System spalania jest wyposażony w regulatory, które kontrolują przepływy gazu pierwotnego i wtórnego w czasie rzeczywistym, na podstawie zmierzonej wartości opałowej.



Rys. 13. Koncepcja proponowanego rozwiązania

Analizując źródła literaturowe nie znaleziono podobnych rozwiązań. W związku z tym, problematyka zagospodarowania uciążliwych dla środowiska gazowych produktów termicznego przetwarzania wybranych odpadów kalorycznych ma charakter aplikacyjny, m.in. ze względu na możliwość zagospodarowania uciążliwych dla środowiska odpadów z tworzyw sztucznych, odpadu RDF oraz bioodpadów, jak i gazowych produktów termicznego przetwarzania tych odpadów. Dodatkowo, cel utylitarny pracy umożliwi obniżenie zużycia gazu ziemnego do opalania pieców grzewczych, co przełoży się na korzyści ekonomiczne.

3.4. Wykorzystanie programu Ansys Chemkin do przewidywania składu spalin

Program Ansys Chemkin-PRO (wersja 2021 R1) służy do analizy chemicznej zjawisk i procesów zachodzących podczas termicznego przetwarzania paliw i odpadów, a model przyjęty do obliczeń nie uwzględnia zjawiska dyfuzji. Podstawą modelu obliczeniowego jest mechanizm chemiczny, który został stworzony przez The Creck Modelling Group. Mechanizm chemiczny opiera się na równaniu stałej szybkości reakcji Arrheniusa (1) [85]:

$$k = AT^b \exp\left(-\frac{E}{RT}\right) \quad (1)$$

gdzie:

A — współczynnik przedwykładniczy (stała przedwykładnicza),

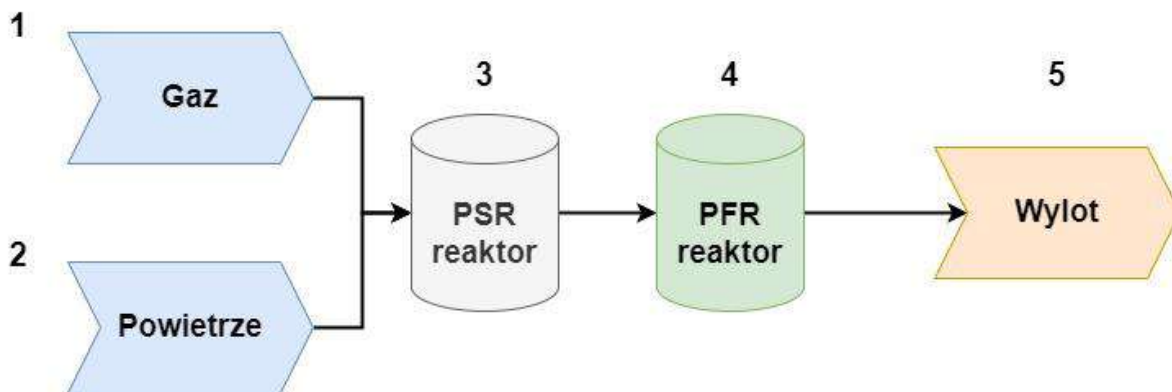
b — wykładnik temperatury,

E — energia aktywacji, J/mol,

R — uniwersalna stała gazowa = 8,314 J/(mol K),

T — temperatura bezwzględna w strefie reakcji, K.

Do obliczeń zaimplementowano szczegółowy mechanizm chemiczny stworzony przez Uniwersytet w Kalifornii, GRI-Mech 3.0 [86], wzbogacony o węglowodory C1-C6, obejmujący dane kinetyczne ponad 60 związków i prawie 350 reakcji chemicznych oraz dane termodynamiczne i transportowe. Do symulacji wykorzystano model oparty na warunku idealnego wymieszania reagentów, tzw. „Perfectly Stirred Reactor - PSR” oraz model z reaktorem z płomieniem swobodnie rozprzestrzeniającym się „The Freely Propagating Flame Reactor - PFR”. Pierwszy model był odpowiednikiem spalania w palniku, natomiast drugi model symulował spalanie w komorze grzewczej ze zdefiniowanym profilem temperatur (rys.14).



Rys. 14. Schematyczny diagram zastosowanego modelu obliczeniowego, gdzie 1 - gaz wlotowy; 2 - powietrze wlotowe; 3 - PSR; 4 - PFR; 5 - wylot.

Ww. program wybrano ze względu na fakt, że według danych literaturowych jest to jeden z najczęściej stosowanych programów, obok ASPEN PLUS, do modelowania zjawisk chemicznych [79,87–89], doświadczenia innych badaczy również potwierdzają stosowanie na szeroką skalę oprogramowania Chemkin v.2021 [90–94].

4. Artykuły stanowiące podstawę do ubiegania się o stopień doktora

4.1. Plastic Waste Management towards Energy Recovery during the COVID-19 Pandemic: the Example of Protective Face Mask Pyrolysis

W artykule zatytułowanym “Plastic Waste Management towards Energy Recovery during the COVID-19 Pandemic: the Example of Protective Face Mask Pyrolysis” przedstawiono ocenę wpływu pandemii COVID-19 na sektor gospodarki odpadami, a następnie na podstawie badań laboratoryjnych i obliczeń komputerowych wskazano, w jaki sposób skutecznie zagospodarować wybrane odpady powstałe w trakcie pandemii. Przeanalizowano odpady pocovidowe, składające się w dużej mierze z odpadów plastikowych. W ramach badań laboratoryjnych określono skład pierwiastkowy. Zhomogenizowany, a następnie sproszkowany materiał z maseczek poddano analizie TGA. Symulacje komputerowe wykonano za pomocą programu Ansys Chemki PRO i prowadzono je w zakresie temperatur 400-900°C dla pilotażowego reaktora pirolitycznego o ciągłym przepływie odpadów 240 kg/h. Wdrożony model obliczeniowy zweryfikowano eksperymentalnie dla warunków procesu pirolizy paliwa odpadowego (RDF).

Wykonane symulacje pozwoliły uzyskać kompleksową wiedzę na temat otrzymanych produktów, w szczególności gazu pirolitycznego. Uzyskana wysoka wartość opałowa gazu pochodzącego z maseczek ochronnych (47,7 MJ/m³) jest zachęcająca, aby wykorzystywać odpady z tworzyw sztucznych w kierunku odzysku energii. Wyniki przeprowadzonych badań i symulacji komputerowych potwierdzają dużą wartość energetyczną odpadów z tworzyw sztucznych. Zwiększenie udziału ww. odpadów w strumieniu odpadów komunalnych, z których wyodrębni się tzw. frakcję przelewową i RDF, spowoduje zwiększenie wartości opałowej gazu pirolitycznego, dzięki czemu jego energetyczne wykorzystanie będzie ekonomicznie opłacalne.

4.2. Numerical and experimental analysis of pyrolysis process of RDF containing a high percentage of plastic waste

W artykule zatytułowanym „Numerical and experimental analysis of pyrolysis process of RDF containing a high percentage of plastic waste” przedstawiono efektywne zarządzanie odpadami komunalnymi w kontekście gospodarki o obiegu zamkniętym. Z powodu panującej w latach 2020-2022 pandemii COVID-19, zmienił się strumień odpadów komunalnych, gdyż wzrósł w nim udział tworzyw sztucznych (maseczki, rękawiczki jednorazowe). W związku z tym, zostały przeprowadzone badania materiałoznawcze, eksperymentalne i obliczenia komputerowe, aby zbadać właściwości paliwa pochodzącego z odpadów (RDF) o wysokiej zawartości tworzyw sztucznych. Jako proces rozkładu termicznego została wybrana piroliza dla tego rodzaju odpadów. Przeprowadzono analizę techniczną i elementarną dla RDF i jego produktów, dodatkowo uzyskany karbonizat został poddany badaniu mikrostrukturalnemu za pomocą skaningowego mikroskopu elektronowego. Pirolizę przeprowadzono przy użyciu reaktora pilotażowego o ciągłym przepływie 250 kg/h w temperaturze 900°C. Do procesu pirolizy zastosowano analizę TGA, której wyniki pokazały, że główny rozpad badanego materiału miał miejsce w zakresie temperatur 250-500°C. Uzyskany w wyniku pirolizy gaz był bogaty w związki takie jak: CO, H₂, CH₄, i C₂H₄, co przełożyło się na wysoką wartość opałową gazu, która osiągnęła 24,4 MJ/m³. Porównując uzyskane wyniki z modelowania z wynikami eksperymentu, obserwuje się dobrą zgodność, o czym świadczy wysoki udział związków palnych, takich jak CO, H₂, CH₄ i C₂H₄, dla wszystkich analizowanych przypadków. RDF powstały z nadsitowej frakcji odpadów, zawierający duże ilości środków ochrony osobistej i innych odpadów wykorzystywanych podczas pandemii (np. opakowania plastikowe) ma duży potencjał energetyczny, ponieważ składa się z plastiku, papieru i tekstyliów. Taki RDF charakteryzuje się wysoką zawartością węgla i wodoru oraz niską zawartością wilgoci, co czyni go surowcem nadającym się do termicznego przetwarzania. Frakcja stała po procesie pirolizy RDF również ma szansę znaleźć swoje zastosowanie w branży energetycznej lub jako substrat do produkcji węgla aktywnego. Gaz pirolityczny o wysokiej wartości kalorycznej (18,4–24,4 MJ/m³) sprzyja szerszemu wykorzystaniu procesu pirolizy odpadów w celu uzyskania paliw wtórnych o obiecujących parametrach energetycznych.

4.3. The role of calorific waste in transformation of iron and steel industry towards sustainable production

W pracy zatytułowanej “The role of calorific waste in transformation of iron and steel industry towards sustainable production” została przedstawiona potrzeba redukcji emisji dwutlenku węgla i osiągnięcia neutralności węglowej w perspektywie 30 lat, ze względu na założenie programu ZeroNet2050. W odpowiedzi na potrzebę redukcji zaproponowano konkretne sposoby na zmniejszenie emisji dwutlenku węgla poprzez dywersyfikację źródeł wykorzystywanej energii z paliw kopalnych na energię pochodzącą z wodoru lub biopaliw. Zaznaczono, że transformacja przemysłu metalurgicznego powinna przebiec ze wsparciem strony rządowej, która będzie oferować np. ulgi podatkowe, dofinansowania i inne benefity finansowe, aby zachęcić przedsiębiorców do szybszego inwestowania w transformację przemysłu stalowego.

4.4. The Application of Lignocellulosic Biomass Waste in the Iron and Steel Industry in the Context of Challenges Related to the Energy Crisis

W artykule zatytułowanym „The Application of Lignocellulosic Biomass Waste in the Iron and Steel Industry in the Context of Challenges Related to the Energy Crisis” została opisana koncepcja zastąpienia węgla kopalnego, biowęgłem pochodzącym z odpadów biomasy lignocelulozowej. Artykuł podsumowuje analizę osiągnięć w badaniach dotyczących wykorzystania produktów biomasy lignocelulozowej w przemyśle hutniczym. Podstawowym założeniem była redukcja emisji dwutlenku węgla (CO₂), poprzez zastąpienie części wykorzystywanego węgla kopalnego, węglem pochodzącym z biomasy. Zaproponowano wykorzystanie biowęgla w procesie wielkopiecowym, w piecu tlenowym oraz w piecu łukowym. Analiza wykazała, że zmniejszenie wykorzystania węgla kamiennego i zastąpienie jego części paliwami pochodzenia biomasowego zmniejszy emisję CO₂ [51,95]. Zgodnie z założonymi szacunkami, zastąpienie 20% koksu biomasą może obniżyć emisję CO₂ o 15% [96]. Światowym liderem w produkcji biowęgla i jego wykorzystaniu w hutnictwie jest Brazylia. Aż 75% wyprodukowanego biowęgla jest wykorzystywane w przemyśle stalowym. Rekomendacje jakie udało się skonstruować po analizie literatury są następujące:

- Zastąpienie nawet niewielkiej części węgla kopalnego biomasą lub biowęgłem przyniesie znaczące obniżenie emisji CO₂ do atmosfery.
- Zracjonalizowane zarządzanie energią przyniesie korzyści ekonomiczne, co przełoży się na większą konkurencyjność na rynku stalowym.
- Zaproponowane rozwiązania są wciąż w fazie testów i badań. Technologia przetwarzania materiałów biomasowych musi zostać dopracowana w jak najwyższym stopniu, aby właściwości, które muszą spełnić biopaliwa odpowiadały wymaganiom technicznym przemysłu stalowego.
- Transformacja energetyczna jest procesem kosztownym i długotrwałym, ale koniecznym, aby zmniejszyć wpływ przemysłu metalurgicznego na środowisko [97,98].

4.5. Possibilities of RDF Pyrolysis Products Utilization in the Face of the Energy Crisis

W artykule zatytułowanym “Possibilities of RDF Pyrolysis Products Utilization in the Face of the Energy Crisis” skupiono się na ocenie możliwości praktycznego wykorzystania produktów pirolizy RDF (gazu pirolitycznego, biowęgla i oleju pirolitycznego), jako alternatywy dla konwencjonalnych paliw kopalnych. Trwający w Ukrainie konflikt zbrojny oraz konieczność transformacji energetycznej przyczyniły się do kryzysu w sektorze energii. Chęć uniezależnienia się od rosyjskich surowców kopalnych oraz rosnąca ilość odpadów komunalnych wymusza wprowadzenie działań opartych na odzysku energii (np. z odpadów). Wychodząc naprzeciw wszystkim powyższym problemom, zaproponowano rozwiązanie polegające na przetwarzaniu w procesie pirolizy odpadu RDF, który ze względu na uwarunkowania legislacyjne jest wytwarzany w dużej ilości, lecz moce przerobowe zakładów przetwarzania termicznego są niewystarczające, aby zagospodarować cały wytworzony RDF. Według danych GUS 1,5-2 mln ton RDF rocznie nie znajduje zagospodarowania. Porównanie 4 metod termicznego przekształcania odpadów (spalania, zgazowania, toryfikacji i pirolizy) wykazało wyższość procesu pirolizy nad innymi metodami, ze względu na elastyczność parametrów procesu, możliwość przetworzenia różnego rodzaju odpadów, stopień odzysku energii na poziomie 80% oraz najniższą emisję zanieczyszczeń takich jak NO_x i CO_2 [72,99,100]. Produkty pirolizy RDF mają również stosunkowo wysoką wartość opałową: dla gazu pirolitycznego średnia wartość wynosi 29,9 MJ/kg, dla karbonizatu 29,1 MJ/kg, a dla oleju pirolitycznego jest to średnia wartość na poziomie 16,5 MJ/kg [8,101,102]. Wartości te śmiało mogą konkurować z wartościami opałowymi paliw kopalnych. Wykorzystanie RDF jest w tym przypadku przykładem rozwiązania pozwalającego na efektywne wykorzystanie odpadów przemysłowych i komunalnych, zmniejszając tym samym ilość odpadów deponowanych na składowiskach i jednocześnie zmniejszając zapotrzebowanie na paliwa kopalne. Wykorzystanie biowęgla lub gazów z termicznego przekształcania odpadów w przemyśle metalurgicznym ma uzasadnienie ekonomiczne [5]. Mimo kosztów inwestycyjnych i adaptacyjnych, jakie przedsiębiorstwa będą musiały ponieść w początkowej fazie transformacji technologicznej, w dłuższej perspektywie może ona przynieść wymierne korzyści dla przemysłu stalowego.

4.6. Methods and Validation Techniques of Chemical Kinetics Models in Waste Thermal Conversion Processes

W artykule zatytułowanym “Methods and Validation Techniques of Chemical Kinetics Models in Waste Thermal Conversion Processes” omówiono potencjał wykorzystania metod symulacji komputerowych w procesach termicznego przekształcania odpadów. Ze względu na wysokie koszty badań eksperymentalnych oraz trudności prowadzenia dużej ilości badań w warunkach rzeczywistych, modelowanie zjawisk termodynamicznych zyskuje na znaczeniu. Symulacje komputerowe pozwalają uniknąć licznych błędów, takich jak te, które mogą wystąpić podczas działań optymalizacyjnych. Ze względu na złożoność zjawisk zachodzących podczas termicznego przekształcania, szczególnie skupiono się na modelach opartych na kinetyce chemicznej, dzięki którym możliwe jest przewidywanie składu ilościowego i jakościowego produktów w tych procesach. Literatura wyróżnia 3 typy podejścia do procesu symulacji: modele obliczeniowe dynamiki płynów [103–105], modele kinetyczne [106–108] i modele równowagi [109–111]. Literatura przedmiotu wymienia dwa główne oprogramowania wykorzystywane podczas symulacji komputerowych do procesów konwersji cieplnej: Aspen Plus i Fluent. Jako dobre narzędzie do przewidywania składu gazowych produktów konwersji cieplnej najczęściej wymienianym oprogramowaniem jest Chemkin (firmy Ansys). Przewagą programów Aspen Plus i Fluent jest prostszy interfejs oraz zastosowanie wielu uproszczeń, ze względu na szeroką gamę badaczy, którzy go wykorzystują (różniący się poziomem specjalistycznej wiedzy). Aby korzystać z programu Chemkin, od użytkowania wymagana jest duża ilość wiedzy specjalistycznej z zakresu kinetyki chemicznej, mechanizmów chemicznych i chemii, co zawęża grono użytkowników, lecz daje możliwość uzyskania bardziej rzetelnych danych.

Oprócz zalet, główną wadą symulacji komputerowych jest możliwość popełnienia błędu przy tworzeniu modelu i trudność w prawidłowej interpretacji wyników symulacji. Problemy te są spowodowane czynnikiem ludzkim. Najlepszą metodą walidacji uzyskanych wyników jest analiza eksperymentalna, którą zaleca się wykonać, mimo potencjalnej dużej zgodności wyników symulacji z wynikami eksperymentu, potwierdzonej przez wielu badaczy [112,113]. Zastosowanie symulacji w procesach termicznego przekształcania odpadów jest szansą na ich szersze wykorzystanie, dzięki



lepszemu zrozumieniu zjawisk zachodzących podczas ich degradacji, zarówno gazodynamicznej, jak i kinetycznej.

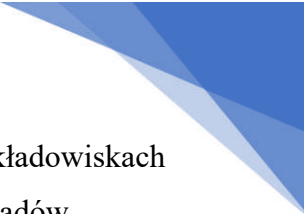
4.7. Analiza mechanizmów chemicznych powstawania uciążliwych dla środowiska produktów spalania gazu z pirolizy odpadów

W artykule zatytułowanym „Analiza mechanizmów chemicznych powstawania uciążliwych dla środowiska produktów spalania gazu z pirolizy odpadów” zbadano wpływ wybranych paramentów (temperatura i czas przebywania) procesu termicznego przetwarzania odpadów, na mechanizmy powstawania uciążliwych dla środowiska produktów gazowych. Symulacje komputerowe wykonano za pomocą programu Chemkin v. 2021. Analizowanym materiałem były gazy pochodzące z pirolizy mieszaniny zrębków sosnowych z polipropylenem (PP) oraz paliwa odpadowego RDF. Poprawność modelu obliczeniowego zwalidowano porównując wyniki dla gazu ziemnego, którego uzyskane obliczenia porównano z wynikami z badania eksperymentalnego. Mechanizm chemiczny, zaimplementowany do programu pochodził z grupy Creck Modeling i obejmował 368 związków oraz 14 462 reakcje. Obliczenia przeprowadzono przy użyciu reaktora o stałej objętości z idealnym wymieszaniem reagentów PSR (perfectly stirred reactor). Wybrany reaktor symulował spalanie wybranych gazów w strefie przypalnikowej. Wyniki symulacji wykazały, że prawidłowy dobór parametrów procesu ma duży wpływ na skład chemiczny uzyskanych produktów. Wydłużony czas przebywania wpływał na wzrost stężenia takich związków jak: NO, N₂O i CO₂ dla wszystkich analizowanych gazów. Zmniejszenie stężenia molowego zaobserwowane w przypadku CO i H₂, które było związane z ich dopalaniem występującym wraz ze wzrostem czasu przebywania. W funkcji temperatury i stałego czasu przebywania (1 ms.), powyżej temperatury 1100°C obserwowano skokowy wzrost stężenia NO dla wszystkich analizowanych gazów, będący skutkiem mechanizmu Zeldowicza, który odpowiada za formowanie tlenków azotu powyżej 1250°C [114]. Przeprowadzone obliczenia komputerowe wykazały, że skład chemiczny produktów gazowych, powstałych ze spalania gazów pirolitycznych, pod względem jakościowym jest bardzo zbliżony do produktów gazowych powstałych ze spalania gazu ziemnego. Wzrost temperatury oraz czasu przebywania w strefie najwyższych temperatur powoduje wzrost stężeń związków: CO₂, N₂O i NO dla wszystkich badanych gazów. Przeprowadzone badania mogą być wartościowym materiałem w przemyśle stalowym, w kontekście zastąpienia paliw kopalnych, paliwami alternatywnymi.

4.8. Prediction of chemical composition of gas combustion products from thermal waste conversion

W artykule zatytułowanym „Prediction of chemical composition of gas combustion products from thermal waste conversion” badano możliwości przewidywania składu gazowych produktów, pochodzących z termicznego przetwarzania odpadów oraz potencjał wykorzystania uzyskanych gazów na cele energetyczne. Globalny kryzys energetyczny wymusza poszukiwanie alternatywnych surowców i paliw, które będą w stanie zapewnić ciągłość funkcjonowania strategicznych gałęzi przemysłu, takich jak przemysł stalowy. Szansą na zmniejszenie zużycia tradycyjnych paliw upatruje się w wykorzystaniu potencjału produktów pochodzących z termicznego przetwarzania odpadów.

W związku z tym, w pierwszej kolejności zostały wykonane badania eksperymentalne, aby móc zwalidować prawidłowość modelu obliczeniowego. Następnie wykonano symulacje komputerowe współspalania gazu pirolitycznego w stosunku 1:10 z gazem ziemnym w strefie grzewczej pieca typu przepychowego, stosowanego do podgrzewania wsadu przed formowaniem na gorąco. Modelowano skład chemiczny spalin powstających podczas spalania samego gazu ziemnego i współspalania z gazem pirolitycznym z różnych odpadów (dwóch rodzajów odpadu RDF oraz mieszanki zrębków sosnowych z polipropylenem oraz mieszanki zrębków olchowych z polipropylenem). Obliczenia wykonano przy użyciu oprogramowania Chemkin v. 2021. Uzyskane wyniki symulacji składu chemicznego produktów gazowych oraz uzyskane ścieżki formowania dla tlenu azotu zostały uzupełnione o analizę czułości szybkości tworzenia poszczególnych związków. Przeprowadzone symulacje komputerowe wykazały, że dodatek gazu pirolitycznego dla większości analizowanych wariantów nie wpłynął znacząco na skład chemiczny spalin. Wyniki najbardziej zbliżone do spalania wyłącznie gazu ziemnego pod względem składu spalin uzyskano w przypadku mieszanki P1 (gaz ziemny + RDF). W przypadku gazów pochodzących z pirolizy odpadów biomasowych z dodatkiem polipropylenu zaobserwowano wyższe stężenia CO i H₂ oraz niespalonych węglowodorów niż w przypadku pozostałych mieszanek (które mają szansę się dopalić w kolejnej strefie pieca). Najważniejszymi wnioskami z badania jest stwierdzenie, że udział na poziomie 10-15% gazu pirolitycznego nie powoduje zwiększenia udziału tlenków azotu w spalinach, co nie będzie skutkowało zwiększeniem



opłat za emisję oraz przyczyni się do zagospodarowania zalegającego na składowiskach odpadu RDF, poprzez utworzenia nowego runku zbytu dla tego rodzaju odpadów.

4.9. Economic Benefits for the Metallurgical Industry from Co-Combusting Pyrolysis Gas from Waste

W artykule zatytułowanym „Economic Benefits for the Metallurgical Industry from Co-Combusting Pyrolysis Gas from Waste” skupiono się na przedstawieniu korzyści, jakie może uzyskać przemysł metalurgiczny, wykorzystując produkty pirolizy w procesach stalowniczych. Zaproponowane rozwiązanie technologiczne polega na umieszczeniu reaktora pirolitycznego przed rekuperatorem pieca przepychowego, co pozwoli na ogrzanie pirolizera do wymaganej temperatury 900°C, bez dostarczania energii z zewnątrz. Następnie pozostałe ciepło będzie wykorzystywane do wstępnego suszenia i ogrzania materiału wsadowego do pirolizera. Uzyskana frakcja gazowa bez schładzania i kondensacji będzie podawana do palników pieca i od razu współspalana z gazem ziemnym. System spalania jest wyposażony w regulatory, które kontrolują przepływy gazu pierwotnego i wtórnego w czasie rzeczywistym, na podstawie zmierzonej wartości opałowej (system stosowany podczas spalania gazu koksowniczego). Do analizy opłacalności wybrano gazy pochodzące z pirolizy mieszaniny odpadów polipropylenowych ze zrębkami biomasowymi. Analiza wykazała oszczędności rzędu ponad 200 tys. euro miesięcznie, przy najwyższej wydajności pieca (90 t/h), oszczędności ponad 400 tys. euro miesięcznie dla wydajności pieca 70 t/h oraz blisko 450 tys. euro oszczędności przy najniższej wydajności pieca, zastępując 11-16% zużycia gazu ziemnego. Analiza opłacalności ekonomicznej NPV wykazała zwrot inwestycji (CAPEX 5 300 000 Euro) już po 3 latach funkcjonowania instalacji we wszystkich przypadkach oprócz najwyższej wydajności pieca (90 t/h). W tym przypadku zwrot powinien nastąpić po 4 latach użytkowania instalacji. Zaproponowane rozwiązanie ma charakter aplikacyjny, dodatkowo zaadaptowanie takiego rozwiązania niesie za sobą szereg korzyści środowiskowych i ekonomicznych. Podsumowując, wykorzystanie odpadów RDF w procesie pirolizy, do produkcji gazu pirolitycznego oraz biowęgla, które w całości zostaną wykorzystane w miejscu produkcji (hucie), przyczyni się do obniżenia kosztów operacyjnych przemysłu stalowego oraz zagospodarowania odpadów, które do tej pory nie znalazły stałego odbiorcy.

5. Podsumowanie i wnioski

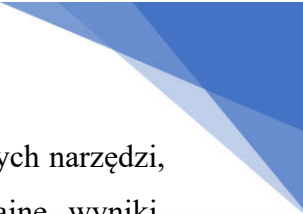
Trwający obecnie kryzys energetyczny wymusza poszukiwanie alternatywnych surowców i paliw, które będą w stanie zapewnić ciągłość kluczowych gałęzi przemysłu, takich jak przemysł stalowy. Szansą na zmniejszenie zużycia paliw kopalnych (np. gazu ziemnego) jest wykorzystanie potencjału gazów pochodzących z termicznego przetwarzania odpadów, a w szczególności gazu pirolitycznego. Niestety, pomimo wysokiej wartości opałowej, gaz ten nie zawsze nadaje się do bezpośredniego, energetycznego wykorzystania. Ograniczeniem jest zbyt wysoka wartość opałowa powstałych produktów gazowych, w szczególności z tworzyw sztucznych, gumy i tekstyliów. Zaproponowana koncepcja wykorzystania gazów pirolitycznych do opalania hutniczego pieca grzewczego typu przepychowego, posiada ograniczenia konstrukcyjne palników, które pozwalają na spalanie gazu o maksymalnej kaloryczności zbliżonej do kaloryczności gazu ziemnego. Z tego powodu gazy pirolityczne o kaloryczności wyższej niż 35 MJ/m^3 nie będą odpowiednim paliwem, dla zaproponowanego rozwiązania. Badania przeprowadzone w cyklu tworzenia powyższych publikacji wykazały, że gazy pirolityczne pochodzące z takich odpadów jak:

- mieszaniny odpadów biomasowych z tworzywami sztucznymi,
- paliwo odpadowe RDF bogate w tworzywa sztuczne, gumę i tekstylia,

wykazują odpowiednie właściwości, aby móc je przekształcać termicznie w instalacjach wytwarzających gaz pirolityczny, z założeniem wykorzystania wszystkich powstałych produktów na terenie jednego przedsiębiorstwa.

Dodatkowo zagospodarowanie obecnie zalegających na składowiskach odpadów RDF, będzie dużym krokiem w kierunku dążenia do uzyskania gospodarki o obiegu zamkniętym. Nowo powstały rynek zbytu dla odpadów takich jak RDF, mieszaniny odpadów komunalnych bogatych w tworzywa sztuczne, które ze względów technologicznych nie zostały poddane innym procesom odzysku, będą mogły zostać wykorzystane w sposób bardziej efektywny, z wysokim wskaźnikiem odzysku energii (sięgającym 80%).

Na podstawie dokonanego przeglądu literaturowego można zauważyć, że modelowanie komputerowe na przestrzeni ostatnich kilkunastu lat przeszło ogromny rozwój. Modele obliczeniowe są coraz bardziej dokładne, co potwierdzają liczne badania laboratoryjne. Wiele światowych ośrodków badawczych ciągle pracuje nad udoskonalaniem warunków brzegowych, mechanizmów chemicznych oraz modeli



numerycznych. Wszystkie te działania mają na celu stworzenia niezawodnych narzędzi, które w krótszym czasie niż badania eksperymentalne, dają miarodajne wyniki, zmniejszając kosztowność wykonywania badań.

Wykonane symulacje komputerowe z użyciem oprogramowania Ansys Chemkion PRO (ver. 2021R1) wykazały duże podobieństwo składu chemicznego w uzyskanych gazach spalinowych pochodzących ze spalania czystego gazu ziemnego, z gazami spalinowymi uzyskanymi ze współspalania gazu ziemnego z uzyskanymi gazami pirolitycznymi. Symulacje komputerowe wykazały, że współspalanie gazu pirolitycznego nie wpływa na zwiększenie emisji tlenku azotu, co mogłoby zwiększyć wysokość opłat klimatycznych. Przeprowadzone symulacje komputerowe mechanizmów chemicznych, odpowiedzialnych za bezpieczne zagospodarowanie gazów do opalania hutniczych pieców grzewczych pod względem środowiskowym i technologicznym wykazały możliwość spalania wybranych gazów pirolitycznych w rozpatrywanej instalacji. Zaadaptowanie takiego rozwiązania wiąże się z instalacją reaktora pirolitycznego do istniejącego ciągu technologicznego, czego możliwości techniczne zostały potwierdzone. Wykonana analiza ekonomiczna wykazała opłacalność takiego rozwiązania, co będzie generowało oszczędnościami rzędu 200-450 tys. euro miesięcznie z tytułu niższego zużycia gazu ziemnego. Analiza opłacalności NPV wykazała zwrot kosztów inwestycji w przeciągu 3-4 lat w zależności od wydajności pracy pieca. Tym samym cel użytkowy jakim było obniżenie kosztów produkcji w przedsiębiorstwie hutniczym poprzez zagospodarowanie gazu powstałego w wyniku termicznego przetwarzania problematycznych odpadów kalorycznych, takich jak: tworzywa sztuczne, tekstylia i guma, przy jednoczesnym wykorzystaniu energii pochodzącej ze spalin do podgrzewania reaktora pirolitycznego został osiągnięty, dzięki zagospodarowaniu np. odpadu RDF, który jest bogaty w ww. odpady.

Oświadczenia współautorstwa

Oświadczam, że w pracy:

- A1. **SKRZYNIARZ Magdalena**, SAJDAK Marcin, ZAJEMSKA Monika, IWASZKO Józef, BINIEK-POSKART Anna, SKIBIŃSKI Andrzej, MOREL Sławomir, NIEGODAJEW Paweł, *Plastic Waste Management towards Energy Recovery during the COVID-19 Pandemic: the Example of Protective Face Mask Pyrolysis*, Energies, 15(7), 2629 (2022), 140 pkt. IF: 3.0.

wkład Pani mgr inż. Magdaleny Skrzyniarz był dominujący i polegał na współtworzeniu koncepcji, opracowaniu metodologii, przeprowadzeniu części symulacji komputerowych (zamodelowaniu dokładnego składu chemicznego gazowych produktów pirolizy), udziale w analizie teoretycznej, dyskusji uzyskanych wyników, częściowym przygotowaniu manuskryptu, przygotowaniu grafik, udziale w przygotowaniu odpowiedzi dla recenzentów.

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Marcin Sajdak

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Monika Zajemska

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Józef Iwaszko

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Anna Biniek-Poskart

.....
Andrzej Skibiński

.....
Sławomir Morel

.....
Paweł Niegodajew



Oświadczam, że w pracy:

A2. ZAJEMSKA Monika, MAGDZIARZ Aneta, IWASZKO Józef, **SKRZYNIARZ Magdalena**, POSKART Anna, *Numerical and Experimental Analysis of Pyrolysis Process of RDF Containing a High Percentage of Plastic Waste*, Fuel, 320, 123981 (2022), 140 pkt. IF: 6.7.

wkład Pani mgr inż. Magdaleny Skrzyniarz polegał na przeprowadzeniu części symulacji komputerowych (zamodelowaniu dokładnego składu chemicznego gazowych produktów pirolizy), udziale w analizie teoretycznej, dyskusji uzyskanych wyników, częściowym przygotowaniu manuskryptu, przygotowaniu grafik, udziale w przygotowaniu odpowiedzi dla recenzentów.

.....
Monika Zajemska

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Aneta Magdziarz

.....
Józef Iwaszko

.....
Anna Biniek-Poskart



Oświadczam, że w pracy:

A3. ZAJEMSKA Monika, SAJDAK Marcin, IWASZKO Józef, **SKRZYNIARZ Magdalena**, BINIEK-POSKART Anna, SKIBIŃSKI Andrzej, MAROSZEK Artur, *The Role of Calorific Waste in Transformation of Iron and Steel Industry Towards Sustainable Production*, Resource, Conservation and Recycling, vol. 191, 106899 (2023), 140 pkt. IF: 11.2.

wkład Pani mgr inż. Magdaleny Skrzyniarz polegał na udziale w analizie teoretycznej, skonstruowaniu wniosków, częściowym przygotowaniu manuskryptu, przygotowaniu grafik.

.....
Monika Zajemska

.....
Marcin Sajdak

.....
Józef Iwaszko

.....
Anna Biniek-Poskart

.....
Andrzej Skibiński

.....
Artur Maroszek



Oświadczam, że w pracy:

A4. BINIEK-POSKART Anna, SAJDAK Marcin, **SKRZYNIARZ Magdalena**, RZĄCKI Jakub, SKIBIŃSKI Andrzej, ZAJEMSKA Monika, *The Application of Lignocellulosic Biomass Waste in the Iron and Steel Industry in the Context of Challenges Related to the Energy Crisis*, Energies, 16(18), 6662 (2023), 140 pkt. IF: 3.0.

wkład Pani mgr inż. Magdaleny Skrzyniarz polegał na współtworzeniu koncepcji, udziale w analizie teoretycznej, dyskusji uzyskanych wyników, częściowym przygotowaniu manuskryptu, przygotowaniu grafik, udziale w przygotowaniu odpowiedzi dla recenzentów.

.....
Anna Biniek-Poskart

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Marcin Sajdak

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Jakub Rzącki

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Andrzej Skibiński

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Monika Zajemska



Oświadczam, że w pracy:

A5. SKRZYNIARZ Magdalena, SAJDAK Marcin, ZAJEMSKA Monika, BINIEK-POSKART Anna, IWASZKO Józef, SKIBIŃSKI Andrzej, *Possibilities of RDF Pyrolysis Products Utilization in the Face of the Energy Crisis*, *Energies*, 16(18), 6695 (2023), 140 pkt. IF: 3.0.

wkład Pani mgr inż. Magdaleny Skrzyniarz był dominujący i polegał na współtworzeniu koncepcji, udziale w analizie teoretycznej, dyskusji uzyskanych wyników, częściowym przygotowaniu manuskryptu, przygotowaniu grafik, udziale w przygotowaniu odpowiedzi dla recenzentów.

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Marcin Sajdak

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Monika Zajemska

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Anna Biniek-Poskart

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Józef Iwaszko

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Andrzej Skibiński



Oświadczam, że w pracy:

A6. SKRZYNIARZ Magdalena, SAJDAK Marcin, BINIEK-POSKART Anna, SKIBIŃSKI Andrzej, KRAKOWIAK Marlena, PIOTROWSKI Andrzej, KRASOŃ Patrycja, ZAJEMSKA Monika, *Methods and Validation Techniques of Chemical Kinetics Models in Waste Thermal Conversion Processes*, *Energies*, 17(13), 3067 (2024), 140 pkt. IF: 3.0.

wkład Pani mgr inż. Magdaleny Skrzyniarz był dominujący i polegał na współtworzeniu koncepcji, udziale w analizie teoretycznej, dyskusji uzyskanych wyników, częściowym przygotowaniu manuskryptu, przygotowaniu grafik, udziale w przygotowaniu odpowiedzi dla recenzentów.

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Marcin Sajdak

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Anna Biniek-Poskart

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Andrzej Skibiński

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Marlena Krakowiak

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Andrzej Piotrowski

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Patrycja Krasoń

.....
Monika Zajemska



Oświadczam, że w pracy:

A7. SKRZYNIARZ Magdalena, RZĄCKI Jakub, Analiza mechanizmów chemicznych powstawania uciążliwych dla środowiska produktów spalania gazu z pirolizy odpadów, *Przemysł Chemiczny*, 103(9), 979-983 (2024), 70 pkt. IF: 0.5.

wkład Pani mgr inż. Magdaleny Skrzyniarz był dominujący i polegał na przeprowadzeniu obliczeń numerycznych (zamodelowaniu dokładnego składu chemicznego gazowych produktów pirolizy), analizie teoretycznej, dyskusji uzyskanych wyników, przygotowaniu manuskryptu, przygotowaniu grafik, udziale w przygotowaniu odpowiedzi dla recenzentów.

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Jakub Rzącki



Oświadczam, że w pracy:

A8. SKRZYNIARZ Magdalena, MOREL Sławomir, RZĄCKI Jakub, Prediction of chemical composition of gas combustion products from thermal waste conversion, Processes, 12(12), 2728 (2024), 70 pkt, IF: 2.8.

wkład Pani mgr inż. Magdaleny Skrzyniarz był dominujący i polegał na współtworzeniu koncepcji, opracowaniu metodologii, przeprowadzeniu symulacji komputerowych (zamodelowaniu dokładnego składu chemicznego gazowych produktów pirolizy), analizie teoretycznej, dyskusji uzyskanych wyników, częściowym przygotowaniu manuskryptu, przygotowaniu grafik, udziale w przygotowaniu odpowiedzi dla recenzentów.

.....
Sławomir Morel

.....
Jakub Rzącki



Oświadczam, że w pracy:

A9. SKRZYNIARZ Magdalena, SAJDAK Marcin, BINIEK-POSKART Anna, SKIBIŃSKI Andrzej, MAROSZEK Artur, NIEGODAJEW Paweł, ZAJEMSKA Monika, *Economic Benefits for the Metallurgical Industry from Co-Combusting Pyrolysis Gas from Waste*, Energy, 133782 (2024), 200 pkt. IF: 9.0.

wkład Pani mgr inż. Magdaleny Skrzyniarz był dominujący i polegał na współtworzeniu koncepcji, opracowaniu metodologii, udziale w analizie teoretycznej, wykonaniu analizy ekonomicznej, dyskusji uzyskanych wyników, częściowym przygotowanie manuskryptu, przygotowaniu grafik, udziale w przygotowaniu odpowiedzi dla recenzentów.

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Marcin Sajdak

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Anna Biniek-Poskart

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Andrzej Skibiński

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Artur Maroszek

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Paweł Niegodajew

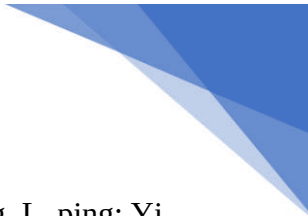
.....
Monika Zajemska



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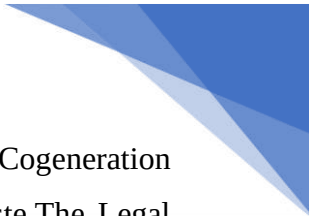
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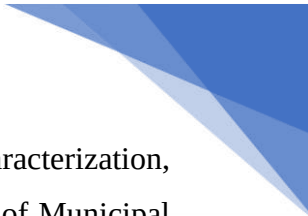
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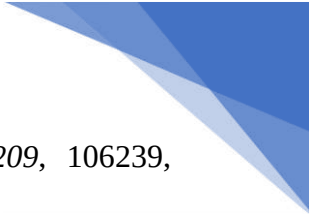
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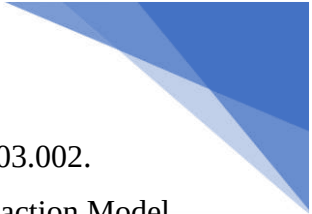
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Załącznik 1 - Wybrane związki zidentyfikowane w analizowanych kondensatach popirolitycznych

Tabela 1a. Wybrane związki zidentyfikowane w analizowanych kondensatach popirolitycznych

RT	Związek	Formula	RDF 3 min	RDF 6 min
2.91	Acetic acid	C2H4O2	3.16%	1.45%
4.17	1,3-Dioxolane, 2,2-dimethyl-	C5H10O2	1.04%	0.85%
7.72	3-Hexen-2-one	C6H10O	0.54%	0.87%
9.89	2-Pentanone, 4-hydroxy-4-methyl-	C6H12O2	1.90%	2.98%
10.80	Ethylbenzene	C8H10	0.29%	0.44%
12.26	Styrene	C8H8	0.93%	0.94%
16.56	2(5H)-Furanone, 3-methyl-	C5H6O2	1.14%	0.73%
16.79	Benzonitrile	C7H5N	0.13%	0.14%
17.17	1-Decene	C10H20	0.21%	0.37%
17.34	Trichloroacetic acid, 6-ethyl-3-octyl ester	C12H21Cl3O2	0.10%	0.00%
19.24	2-Cyclopenten-1-one, 2,3-dimethyl-	C7H10O	0.16%	0.13%
21.00	Benzaldehyde, 3-methyl-	C8H8O	0.44%	0.57%
23.75	Phenol, 2,4-dimethyl-	C8H10O	0.80%	0.15%
24.19	Naphthalene, 1,2,3,4-tetrahydro-	C10H12	1.69%	0.92%
24.85	Benzoic acid	C7H6O2	3.23%	6.11%
25.82	Phenol, 2,4,6-trimethyl-	C9H12O	0.32%	0.11%
27.54	Acetic acid, chloro-, decyl ester	C12H23ClO2	0.00%	0.11%
28.97	1-Tridecene	C13H26	0.26%	0.39%
29.47	1-Undecene, 7-methyl-	C12H24	0.18%	0.41%
29.79	1,2-Benzenedicarboxylic acid	C8H6O4	0.91%	0.37%
29.95	Benzene, (3-chloro-3-methylbutyl)-	C11H15Cl	0.00%	0.16%
30.48	Benzenebutanenitrile	C10H11N	0.55%	0.18%
31.94	Naphthalene, 2-ethenyl-	C12H10	0.30%	0.47%
32.32	Tetradecane	C14H30	0.40%	0.60%
33.25	Naphthalene, 1,3-dimethyl-	C12H12	0.18%	0.15%
33.34	Pyrrole, 2-methyl-5-phenyl-	C11H11N	0.16%	0.21%
33.68	Diphenylmethane	C13H12	0.23%	0.35%
35.47	1-Pentadecene	C15H30	0.53%	0.89%
36.92	Benzene, (3-chloroallyl)-	C9H9Cl	0.00%	0.17%
37.26	Trichloroacetic acid, tetradecyl ester	C16H29Cl3O2	0.14%	0.16%
38.24	Fluorene	C13H10	0.81%	0.96%
38.45	1-Hexadecene	C16H32	1.16%	4.02%
38.66	Hexadecane	C16H34	0.00%	0.32%
39.61	Benzophenone	C13H10O	0.48%	0.48%
40.24	Benzene, 1,1'-(1,3-propanediyl)bis-	C15H16	2.58%	0.76%
41.08	1,16-heptadecadiene	C17H32	1.41%	1.14%

41.27	1-Heptadecene	C17H34	1.72%	1.92%
41.47	Heptadecane	C17H36	0.00%	0.36%
41.80	Ethylene, 1,1-diphenyl-	C14H12	0.68%	0.37%
42.06	Naphthalene, 1-(1-cyclohexen-1-yl)-	C16H16	0.51%	0.45%
42.48	1,2-Diphenylcyclopropane	C15H14	1.72%	1.06%
42.55	Cyclopentane, (2-hexyloctyl)-	C19H38	0.88%	1.11%
43.70	Phenanthrene	C14H10	1.34%	0.90%
43.78	1,17-Octadecadiene	C18H34	1.10%	0.99%
43.95	1-Octadecene	C18H36	2.33%	2.10%
44.13	Octadecane	C18H38	0.39%	0.34%
44.27	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	C16H16	1.32%	0.48%
45.76	Naphthalene, 1-phenyl-	C16H12	1.21%	0.79%
46.35	1,18-Nonadecadiene	C19H34	0.90%	0.88%
46.51	1-Nonadecene	C19H36	2.01%	2.01%
46.66	1H-Cyclopropa[l]phenanthrene, 1a,9b-dihydro-	C15H12	0.90%	0.77%
46.83	1-Methyl-3-phenyl-1H-indene	C16H14	1.47%	0.80%
48.54	Naphthalene, 2-phenyl-	C16H12	3.84%	1.21%
48.81	1,19-Eicosadiene	C20H38	0.87%	0.68%
48.95	1-Eicosene	C20H40	1.66%	1.57%
49.07	Eicosane	C20H42	0.86%	0.62%
49.80	11,13-Dimethyl-12-tetradecen-1-ol acetate	C18H34O2	0.70%	0.67%
51.15	1,20-heneicosanediene	C21H40	0.91%	0.79%
51.29	1-Heneicosene	C21H42	1.73%	1.78%
51.41	Heneicosane	C21H44	0.28%	0.38%
52.65	m-Terphenyl	C18H14	0.52%	0.12%
52.99	1-Hexacosanol	C26H54O	0.43%	0.58%
53.20	Phenol, 4,4'-(1-methylethylidene)bis-	C15H16O2	0.58%	2.28%
53.41	1,19-docosadiene	C22H42	0.64%	0.63%
53.52	1-docosene	C22H44	1.88%	1.92%
53.64	docosane	C22H46	0.24%	0.24%
54.16	Retene	C18H18	0.23%	0.27%
55.56	1,22-Tricosadiene	C23H44	0.73%	0.65%
55.67	1-tricosene	C23H46	1.25%	1.35%
55.78	Tricosane	C23H48	0.20%	0.30%
57.12	Methyl 3,7,11,15-tetramethylhexadec-2-enoate	C21H40O2	0.67%	1.22%
57.52	Z-9-Pentadecenol	C15H30O	0.24%	0.22%
57.73	1-tetracosene	C26H54O	1.60%	0.91%
59.71	1-pentacosene	C25H50	0.82%	1.17%
61.32	pentacosane	C25H52	0.00%	0.14%
65.23	1-Hexacosene	C26H52	1.92%	1.41%
66.95	Carbonic acid, octadecyl 2,2,2-trichloroethyl ester	C21H39Cl3O3	1.87%	1.32%



Załącznik 2 – Artykuły składające się na cykl publikacji

Article

Plastic Waste Management towards Energy Recovery during the COVID-19 Pandemic: The Example of Protective Face Mask Pyrolysis

Magdalena Skrzyniarz ¹, Marcin Sajdak ² , Monika Zajemska ¹ , Józef Iwaszko ¹ , Anna Biniek-Poskart ³ , Andrzej Skibiński ³ , Sławomir Morel ¹ and Paweł Niegodajew ^{4,*} 

- ¹ Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology, 19 Armii Krajowej Avenue, 42-200 Czestochowa, Poland; magdalena.skrzyniarz@pcz.pl (M.S.); monika.zajemska@pcz.pl (M.Z.); jozef.iwaszko@pcz.pl (J.I.); slawomir.morel@pcz.pl (S.M.)
- ² Department of Air Protection, Faculty of Energy and Environmental Engineering, Silesian University of Technology, 22 B Konarskiego Avenue, 44-100 Gliwice, Poland; marcin.sajdak@polsl.pl
- ³ Faculty of Management, Czestochowa University of Technology, 19 B Armii Krajowej Avenue, 42-200 Czestochowa, Poland; anna.poskart@pcz.pl (A.B.-P.); andrzej.skibinski@pcz.pl (A.S.)
- ⁴ Faculty of Mechanical Engineering and Computer Science, Czestochowa University of Technology, 21 Armii Krajowej Avenue, 42-200 Czestochowa, Poland
- * Correspondence: pawel.niegodajew@pcz.pl; Tel.: +48-34-32-50-537

Abstract: This paper presents an assessment of the impact of the COVID-19 pandemic on the waste management sector, and then, based on laboratory tests and computer calculations, indicates how to effectively manage selected waste generated during the pandemic. Elemental compositions—namely, C, H, N, S, Cl, and O—were determined as part of the laboratory tests, and the pyrolysis processes of the above wastes were analysed using the TGA technique. The calculations were performed for a pilot pyrolysis reactor with a continuous flow of 240 kg/h in the temperature range of 400–900 °C. The implemented calculation model was experimentally verified for the conditions of the refuse-derived fuel (RDF) pyrolysis process. As a result of the laboratory tests and computer simulations, comprehensive knowledge was obtained about the pyrolysis of protective masks, with particular emphasis on the gaseous products of this process. The high calorific value of the pyrolysis gas, amounting to approx. 47.7 MJ/m³, encourages the management of plastic waste towards energy recovery. The proposed approach may be helpful in the initial assessment of the possibility of using energy from waste, depending on its elemental composition, as well as in the assessment of the environmental effects.

Keywords: plastic waste; waste management; pyrolysis; thermal conversion; protective mask



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1. Introduction

The appearance and rapid spread of the SARS-CoV-2 virus have caused an intensive increase in the demand for personal protective equipment, especially face masks, due to the obligation to wear them in public spaces [1]. The production of disposable food packaging has also significantly risen during the pandemic [2]. Quarantine, isolation, and the fear of a personal visit to the store have caused an increase in online sales of food, as well as other products necessary in everyday life [3,4]. For practical and hygienic reasons, many of these items are packed in disposable plastic packaging [5,6]. The necessity to ship the ordered products involves the use of cardboard boxes, packaging, cling film, bubble wrap, etc. to safely deliver the ordered products [7]. In addition, shoppers are encouraged to wear disposable gloves and to pack all fresh produce separately in plastic bags when shopping in stationery stores [8,9]. The consequence of this state of affairs is, unfortunately, an enormous increase in the amount of plastic waste, which, as of 22 November 2020, in the 25 countries with the highest incidence of COVID-19, reached approximately 54,000 tons [10]. This

situation was also reflected in the production of the European plastics industry, especially in the second half of 2020.

The presented data show that the production of plastics before the COVID-19 pandemic increased until 2018 and with it the amount of plastic waste (Figure 1). In contrast, the production of the European plastics industry has decreased since 2018. However, after a sharp decline in production due to the restrictions resulting from the COVID-19 pandemic in the first half of 2020, in the second half of this year, the production of plastics in EU countries began to increase rapidly, according to the Association Plastics Manufacturers in Europe (Plastics Europe) and the European Association of Plastics Recycling and Recovery Organisations (EPRO).

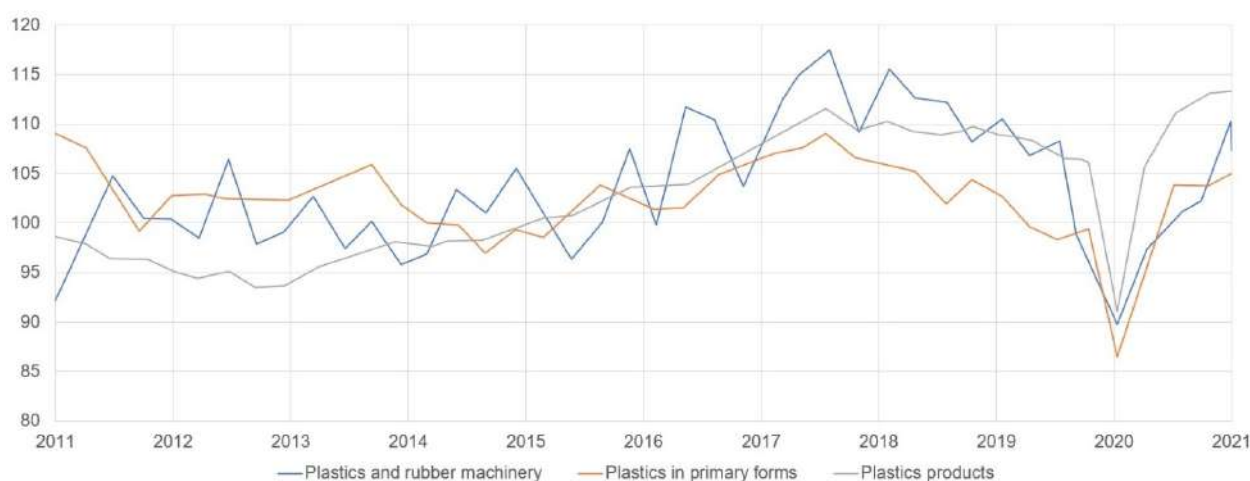


Figure 1. Plastic industry production in EU27 (index 2015 = 100, seasonally adjusted quarterly data) [11].

The pandemic has also had a negative impact on the economy and the proper functioning of local governments [12]. Municipalities and cities are struggling with an augmenting amount of municipal solid waste (MSW) [13] and medical waste, with a simultaneous lower budgetary inflow of funds as a result of the economic downturn [14]. Local governments cannot adequately manage the growing amount of hazardous waste placed in municipal landfills because of a lack of forces and resources at their disposal [15]. It should be noted that the challenges associated with plastics are largely owing to the fact that the ways in which such plastics are produced and utilised are not sustainable, because personal protective equipment (PPE) for hygiene reasons cannot be reusable, recycled, or are often made of single-use plastic. There is no doubt that the COVID-19 pandemic has changed the production and use of plastics [16]. These plastics significantly contribute to limiting the spread of the virus [12]. Nonetheless, according to the authors of this publication, the rapid increase in plastic waste due to the widespread use of masks and gloves, as well as changes in the manufacture and use of disposable products, could, in the short term, undermine EU efforts to reduce plastic pollution and move to more sustainable plastic handling [17,18].

The shock of the outbreak and expansion of the virus on a global scale poses enormous challenges to economies, public finances, and health systems with the threat of a possible recession [19]. The solid waste management sector is particularly susceptible, especially in EU countries, including Poland, which do not meet the requirement of recycling 50% of municipal waste (in 2020, recycling of MSW amounted to 26.7%, according to GUS data) [20,21]. Taking the example of Poland, it can be seen that during the pandemic there was a clear slowdown in the amount of processed waste, resulting in lower incomes in waste management treatment (WMT). Moreover, the situation in the secondary raw materials market had a negative impact on the entire waste industry. The prices of new commodities also fell, which resulted in their greater demand. On the other hand, the waste-to-energy industry (WTE) achieved good ratings and results. For example, the solid

waste disposal sector in the Chinese market did not experience large deviations from the turnover recorded in 2019 [22].

The demand for personal protective equipment (PPE) has grown enormously worldwide since the start of the pandemic [23]. Such a high demand for PPE has led to the generation of huge amounts of plastic waste. For example, in Singapore, during 2 months of lockdown, an additional 1400 tons of plastic was generated [24]. Estimated calculations performed by Sazzadul Haque et al. [25] in Bangladesh have resulted in forecasts that the combined production of disposable face masks and other personal protective equipment is 3.4 billion units per month. This, in turn, translates into the production of 472.3 tons of plastic waste. According to estimates provided by Benson et al. [26], in Africa alone, assuming that people used at least one mask every day, it is estimated that the number of masks produced and disposed of during the day per person is around 412 million. Thus, more than 12 billion medical or textile masks are thrown away every month. Assuming that the average mass of the mask is 8.58 g, this gives the probability that about 105 Mt of masks per month only on the African continent may be discharged into the environment. According to Aragaw et al. [27], each month, around 129 billion masks and 65 billion disposable gloves are used and discarded worldwide.

The waste produced during the pandemic mainly consists of plastics such as polypropylene (PP), polyethylene (PE), polyester (PEs), polycarbonate (PC), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and high-density polyethylene (HDPE), in addition to a small amount of paper, textiles, cotton, and natural rubber (Table 1) [28,29]. As can be seen from the literature review (Table 1), plastic waste can be a valuable fuel due to its high calorific value (38–46 MJ/kg).

Table 1. Proximate and ultimate analysis of plastic waste.

Plastic	Proximate Analysis (wt% Dry Basis)		Elemental Analysis (wt% Dry Basis)					LHV (MJ/kg)	Source
	Volatile Matter	Ash	C	H	N	S	O		
HDPE	98.2	1.8	84.5	13.8	0.1	0.1	1.5	43.0	[30]
LDPE	99.8	0.0	86.8	12.9	0.1	-	0.2	43.6	
PP	99.6	0.4	85.0	13.9	0.1	0.0	1.0	43.6	
PS	99.8	0.1	90.5	7.9	0.4	0.2	1.0	38.8	
PET	92.9	6.9	62.5	4.0	0.1	0.0	33.5	21.1	
PET-12	-	4.9	77.1	12.6	0.2	-	5.2	-	[31]
PET-28	-	12.1	67.2	9.7	0.1	-	10.9	-	
PET	86.75	6.83	63.94	4.52	0.01	0.04	31.49	-	[32]
PS	98.81	-	92.2	7.8	-	-	-	41.25	[33]
PE	99.96	-	85.5	14.5	-	-	-	-	
HDPE	91.88	3.9	83.4	12.71	1.08	0.002	2.8	46.48	[34]
PP	93.84	3.68	83.28	13.81	1.01	0.001	1.90	44.43	
PS	94.33	0.84	89.2	8.78	0.01	0.00	2.01	40.34	

“-” No data available.

Disposable face masks account for a significant share of the plastic waste stream generated during the pandemic [35]. As reported by Benson et al., the global production of disposable face masks is around 1.6 million tons/day, which means around 3.4 billion are thrown away daily due to the COVID-19 pandemic [26]. Protective masks are made of heterogeneous material, i.e., they consist mainly of several layers of PP and PE [36] (and additionally, they are equipped with an elastic band for the ears and a stiffening wire on the nose), which hinders their safe and quick recycling [37,38].

The most appropriate method of neutralising PPE should be material recycling, but due to the difficulty of separating the individual layers from each other, it would be a very time-consuming process [39]. Considering all the emerging difficulties that may arise in the recycling of PPE, one of the most effective methods of their disposal is the thermal transformation process [40–42]. Thus, effective waste management is a global concern

that necessitates a reassessment of current technology and solutions. [43]. According to the introduced regulations, among others in Poland, waste generated during a pandemic and ending up in the mixed waste stream should be thermally neutralised by incineration, pyrolysis, or gasification [44,45]. In addition, mobile installations using the method of the thermal conversion of waste, i.e., pyrolysis, may occur to be an effective solution that responds to the needs of the waste industry during the pandemic. Mobile installations could be successfully utilised by entities collecting waste during the COVID-19 epidemic to neutralise hazardous (infectious) waste directly at the place of its collection, thus minimising the risk to public health and the environment. The above solution may also be used in the case of municipal waste contaminated with a biological agent from quarantine facilities and from places of isolation of patients at home. For the safe disposal of post-COVID-19 waste, a novel and sustainable approach is needed. As indicated in the literature, one of the most perspective methods of the thermal conversion of solid municipal waste, including plastic waste is pyrolysis, which can be a promising route to sustainable waste management. It is a thermochemical process carried out in the absence of oxygen in a pyrolysis reactor, in which waste decomposes at a temperature of 400–900 °C. This method enables the effective neutralisation of hazardous waste, but also leads to the formation of valuable solid (char) and gaseous (high-calorific pyrolysis gas) products that can be used, thus reducing the total cost of pyrolysis. The share and quality of individual products varies, depending, among others, on the type of pyrolysis reactor, type of waste, temperature, and residence time in the reactor [45].

The advantage of a pyrolysis installation compared with a waste incineration plant is its greater flexibility in terms of the amount of processed waste. These installations are economically justified also in the case of disposing of smaller amounts of waste than in the case of incineration plants, which gives opportunities, for example, to small municipal corporations operating, among others, in Polish conditions, for effective and profitable solid waste management. The proposed disposal method is also characterised by lower financial outlays and environmental fees, compared with incineration plants, as well as lower emissions of pollutants, i.e., SO₂ and NO_x. Hence, pyrolysis is considered to be a sustainable solution that may be economically profitable on a large scale and could minimise environmental concerns [46]. According to available data, with the limited number of possible solutions in this area, there is a great need for innovation enabling it to meet the key challenges in the field of plastic waste management in the pandemic era and to integrate new solutions in the field of thermal waste treatment technologies into the existing waste management system.

Taking into account above mentioned facts, pyrolysis seems to be the most promising thermal conversion method for such kind of waste into an environmentally inert, as well as valuable product from the energy point of view. Furthermore, considering the latest research results obtained by the authors of the article [47], in the case of RDF pyrolysis, it is justified to develop pyrolysis technology with simultaneous management of the products of this process.

Pyrolysis gas's high calorific value (30 MJ/m³) encourages its use in both heating and the iron and steel industry. The gas produced by RDF pyrolysis can be co-incinerated with natural gas in industrial heating chambers, reducing the consumption of that fossil fuel. Pyrolysis gas can also be a substitute for coke oven gas for heating furnaces. This gas could be a viable alternative to conventional fuels, helping to reduce the role of waste storage while also improving environmental protection. The liquid fraction, in turn, is a potential source of valuable chemicals such as benzene and toluene. It can also be used as liquid fuel with properties similar to fuel oil or diesel fuel. Moreover, the preliminary technological tests carried out by the authors have shown the possibility of using the solid pyrolysis product in the production of insulating building materials, which increases the economic attractiveness of pyrolysis compared with other methods, e.g., combustion.

Bearing in mind the above, the authors of this study undertook this study to assess the impact of the COVID-19 pandemic on the waste management sector and to identify an effective method of managing selected waste generated during the pandemic.

2. Materials and Methods

The subject of the research was non-medical, three-layer, biologically uncontaminated disposable face masks presented in Figure 2, produced by Quanzhou Ruoxin Hygiene Products Co. Ltd. Caicuo, Luoyang, Huian Country, Quanzhou City, Fujian Province, China, manufactured according to the GB/T 32610-2016 standard, model NS-2020.

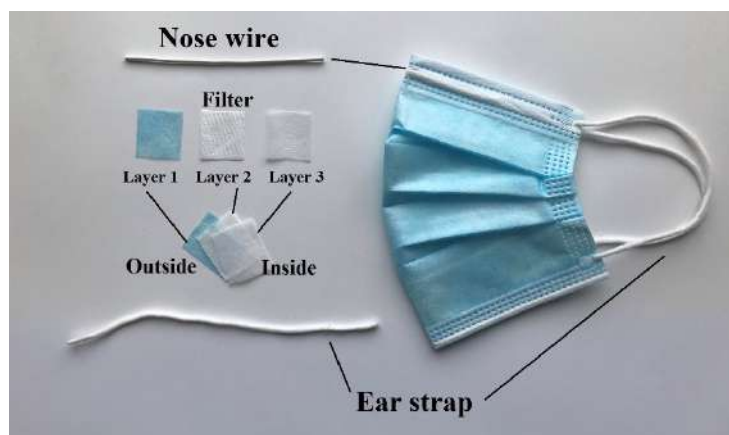


Figure 2. View of disposable protective mask used for studies.

As part of the research, both laboratory experiments and computer simulations were carried out. The research scheme is shown in Figure 3.

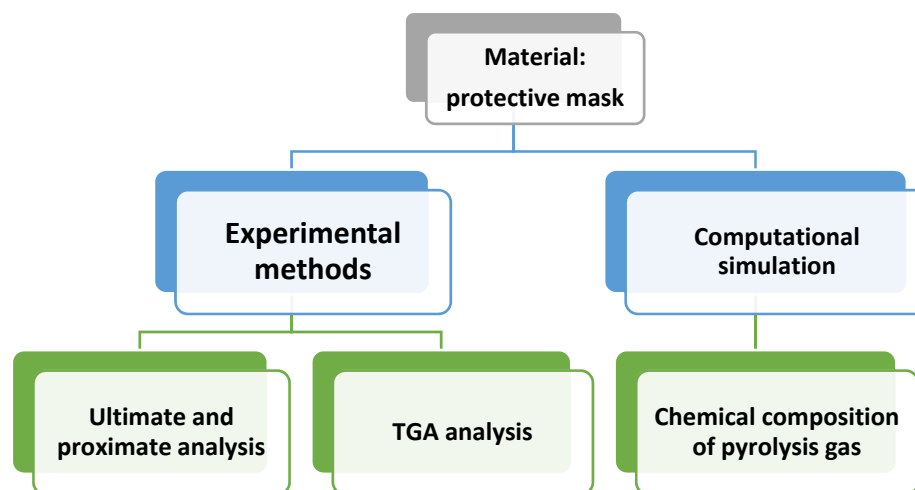


Figure 3. Research scheme.

2.1. Experimental Procedures

2.1.1. Proximate Analysis

Proximate analysis, e.g., the total moisture and ash content, were determined in the studied material. The total moisture content was determined by drying a sample in a laboratory dryer to a constant weight at 105 ± 3 °C. The ash content of the samples was determined by sample incineration. The investigated sample was put in a muffle furnace and heated in an air atmosphere at 600 ± 10 °C. This temperature was maintained until the sample reached a constant weight [48].

2.1.2. Ultimate Analysis

The elementary C_t^a , H_t^a , N^a , S_t^a , and O_t^a compositions in the examined material (protective mask) were measured using a Vario MACRO Cube automatic elemental analyser [49]. At 1150 °C, the material was put through an automated quantitative combustion process in an oxygen stream. Then, the combusted gases were transferred to a reduction tube (filled with copper) in which the sulphur and nitrogen oxides were reduced to SO_2 and N_2 . The combustion gases were sent to a dynamic separation system after passing through the reduction tube. The absorption columns were desorbed thermally in order in the separation system. A thermal conductivity detector was used to identify gases including N_2 , CO_2 , H_2O , and SO_2 (TCD). An NDIR detector was used to examine low SO_2 concentrations [47].

The oxygen concentration was measured quantitatively using sample pyrolysis at 1120–1150 °C in an H_2O -, CO_2 -, and O_2 -free reductive environment (95% N_2 and 5% H_2). The sample was put in a pyrolysis tube containing elemental carbon, and carbon dioxide was produced as a result of the interaction between the oxygen in the sample and the carbon in the filler (Boudouard equilibrium). Granulated NaOH absorbed the acidic compounds obtained during the pyrolysis process, such as H_2S , HCN, and HCl, while a dehumidifier absorbed the generated water. The other gases did not need to be separated because the NDIR detector was only sensitive to CO. The inert pyrolysis products (N_2 and CH_4) might be immediately transported into a carbon monoxide measuring device.

2.1.3. Chlorine Determination

The chlorine content in the studied sample was determined by a potentiometric method [50]. The approach involves thoroughly burning a sample in an oxygen bomb calorimeter with an Eschka mixture (MgO and Na_2CO_3 , ratio 2:1). The generated chlorides (combustion products) were extracted in nitric acid (V) and titrated for chloride ions with 0.1 mol/L $AgNO_3$. The potentiometric titration method used a silver sulphide electrode with a potential that was dependent on that of a reference electrode. The concentration of chloride ions is measured by the potential difference between the electrodes.

3. Results and Discussion

The results of the above-mentioned studies are summarised in Table 2.

Table 2. Proximate and ultimate analysis of plastic waste of protective masks.

Material	Proximate Analysis (wt% Dry Basis)					Elemental Analysis (wt% Dry Basis)			
	Ash	Moisture	Voltaire Matter	C	H	N	S	O	Cl
Plastic waste of protective mask	4.76	1.23	95.24	76.4	11.65	1.12	0.16	4.65	0.03

3.1. TGA Analysis

The tested material (protective mask) was homogenised and then pulverised with a cryogenic mill for thermogravimetric analysis. A Luxx 409 PG thermogravimetric analyser was used in conjunction with a Netzsch QMS 403D Aëolos mass spectrometer. The experiments were conducted in an argon environment with a 25 mL/min flow rate. Measurement began at a temperature of 40 °C. During the research, water jacket testing was used to stabilise the equilibrium. The pyrolysis operations reached a maximum temperature of 700 °C. The sample was 5.0 0.1 mg in weight. The samples were put in 6 mm diameter Al_2O_3 crucibles. The mass loss (TG) and maximum rate of mass loss (DTG) during the reaction, as well as the beginning and final temperatures at each step of the pyrolysis processes, could all be calculated using the data acquired (Figure S1 in Supplementary Material). To illustrate the differences between the various materials, in Figure 3, in addition to the protective mask test sample, the results of thermogravimetric analysis for pure

polypropylene and pure polyethylene terephthalate are shown, as well as three biomass samples [49].

3.2. Computational Simulation

Calculations were made for the pyrolysis process carried out in a pilot continuous pyrolysis reactor, described in detail in [47], using licensed Ansys CHEMKIN-PRO software. Surgical masks with the elemental composition presented in Table 2, as well as PET and PP, the elemental composition of which were taken from studies of [51] and [49] were analysed. A detailed mechanism for the thermal conversion of solid fuels was implemented for the calculations, based on the Arrhenius equation for the rate constant of a reaction [52], developed by the CRECK Modeling Group, including 169 compounds and 4656 chemical reactions [53]. The mechanism was based on the detailed mechanism of HCl and Cl₂ high-temperature chemistry reported in [54]. The chemical mechanism adopted for calculations has been used many times by Ranzi [55,56], Faravelli [57], as well as by the authors of this article to model the thermal conversion of fuels and waste [47,58,59]. The calculations assume that pyrolysis occurs in a reactor with perfect reactant mixing, i.e., a perfectly stirred reactor (PSR) [60]. A diagram of the performed calculations with the input data and the conditions of the pyrolysis process is shown in Figure 4.

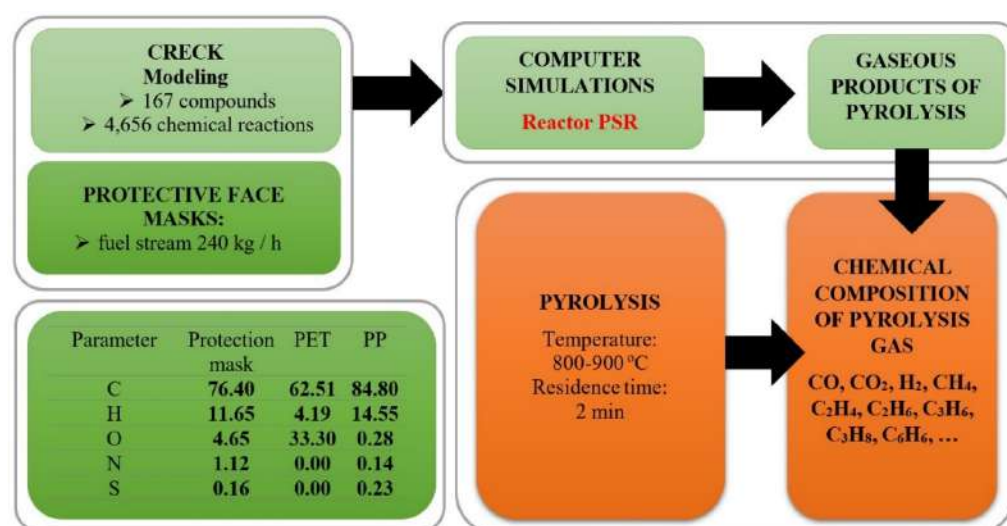


Figure 4. Scheme of calculation procedure.

As part of the computer simulations, the chemical composition of the gaseous pyrolysis products of the above-mentioned waste was determined, on the basis of which the calorific value of the pyrolysis gas was calculated. The following compounds were analysed in detail: CO, CO₂, H₂, CH₄, C₃H₈, C₄H₄, C₆H₆, C₂H₂, C₂H₄, C₂H₆, and C₃H₆. The obtained results were compared with the experimental data obtained from RDF pyrolysis with a high content of plastic waste (over 60%).

3.3. TGA Analysis

Thermogravimetric analysis (TGA) quickly shows the subsequent phases of the thermal conversion process of the studied sample. The mass loss of the examined material during heating is explained by this analysis. The TGA function's second derivative, which is mass change as a function of temperature (DTG), is used to determine the temperature at which the decomposition rate (in the considered example) is highest. The type of studied material is determined by the temperature and the shape of the DTG curve (e.g., one small and sharp peak or a wide peak).

The outcomes of the obtained repetitions are comparable, as can be shown (Figure 5.).

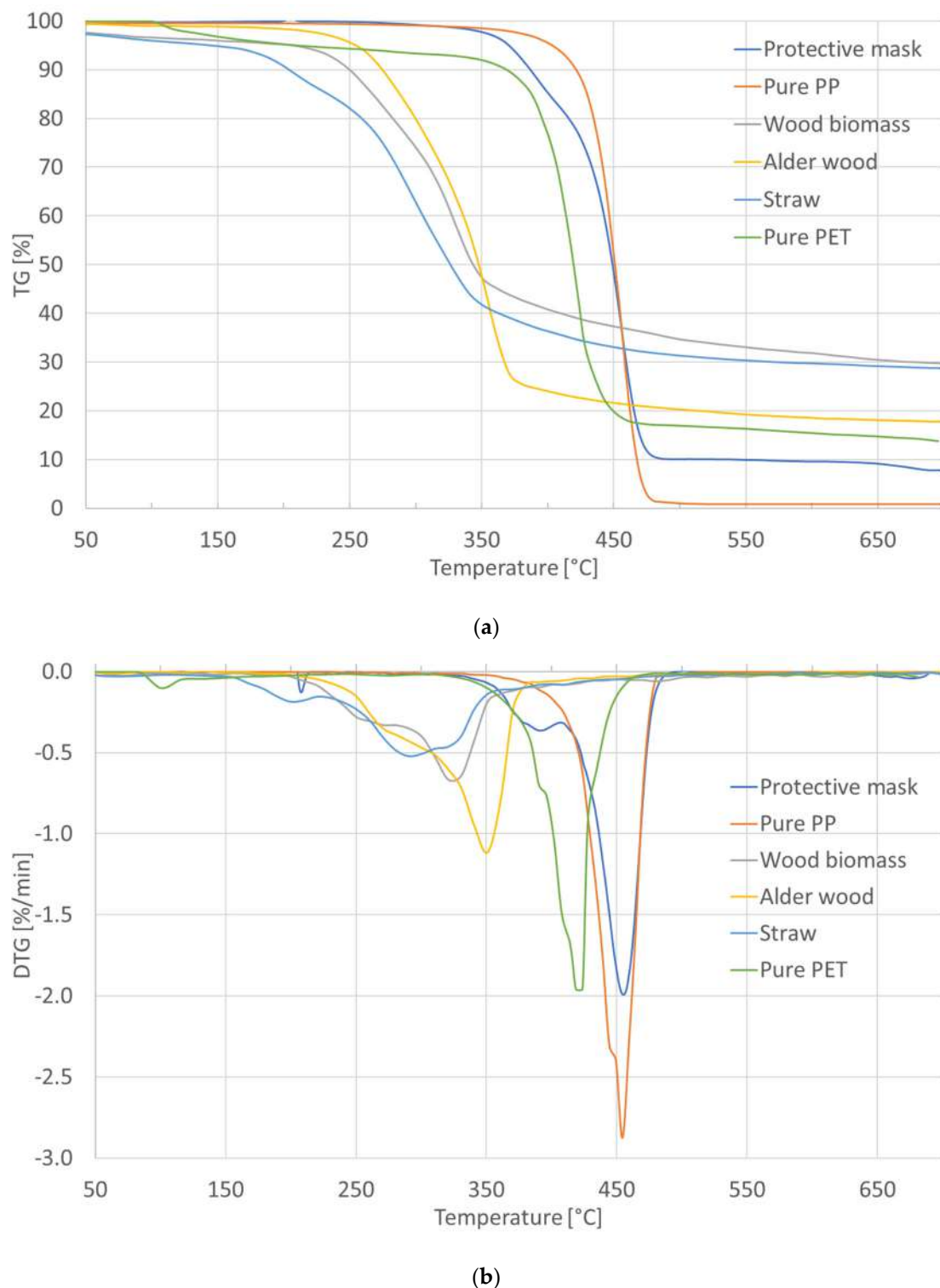


Figure 5. Comparison of repeated TG curves (a) and the TG and DTG curve (b).

As a result, further research may be conducted.

To optimise the number of gaseous products generated during the pyrolysis process, thermogravimetric analysis was carried out at a final temperature of 700 °C for the TGA analysis and 900 °C for the TGA-MS study. The face mask might degrade in four stages, according to TGA data (Figure 4).

The temperature ranges for the four stages were 50–200 °C, 201–392 °C, 393–500 °C, and 501–700 °C. The first stage represents minor degradation regions due to the occurrence

of moisture evaporation (~2 wt%). The second stage indicates the sample's first substantial decomposition zone, with a mass loss of 16.11 wt% due to organic material degradation below 392 °C, caused by the release of pyrogenetic water from the research material made from polypropylene and a melt blown filter (PP). The third stage represents the second major decomposition region of the investigated sample, with a mass loss of 72.55 wt%, owing to the decomposition of organic materials below 455 °C, which corresponds to polypropylene thermoplastic material [61]. The last decomposition stage represents minor degradation regions due to char devolatilisation/decomposition (~2 wt%). The decomposition of the mineral portion present in the sample, magnesite (MgCO_3), which is used as a filler in polymer processing, is connected with the DTG peak detected at 677.6 °C in this location. The DTG curve (Figure 6) shows that the components included in the material from which the investigated face mask were made decompose into two main components (two major degradation peaks), but both corresponded to PP pyrolysis products. During the decomposition of the polypropylene portion at 403.8 °C, one of the most significant emissions of gaseous chemicals from the examined sample is detected—pyrogenetic water (m/z 18) and carbon dioxide (m/z 44). The gaseous fraction, rich in alkanes ($\text{C}_n\text{H}_{2n+1}^+$), alkenes ($\text{C}_n\text{H}_{2n-1}^+$), is observed at a higher temperature of 455.3 °C during the pyrolysis process. They correspond to the mass ions at m/z 43, 55, 56, 57, 69, and 70, respectively, for C_3H_7^+ , C_4H_7^+ , C_4H_8^+ , C_4H_9^+ , C_5H_9^+ , and $\text{C}_5\text{H}_{10}^+$. The mass ion m/z 53 corresponds to $\text{C}_3\text{H}_3\text{N}^+$, which may come from the degradation of a pigment added to the plastic material of one side of the mask. The results from mass spectrometry are shown in Figures 6 and 7.

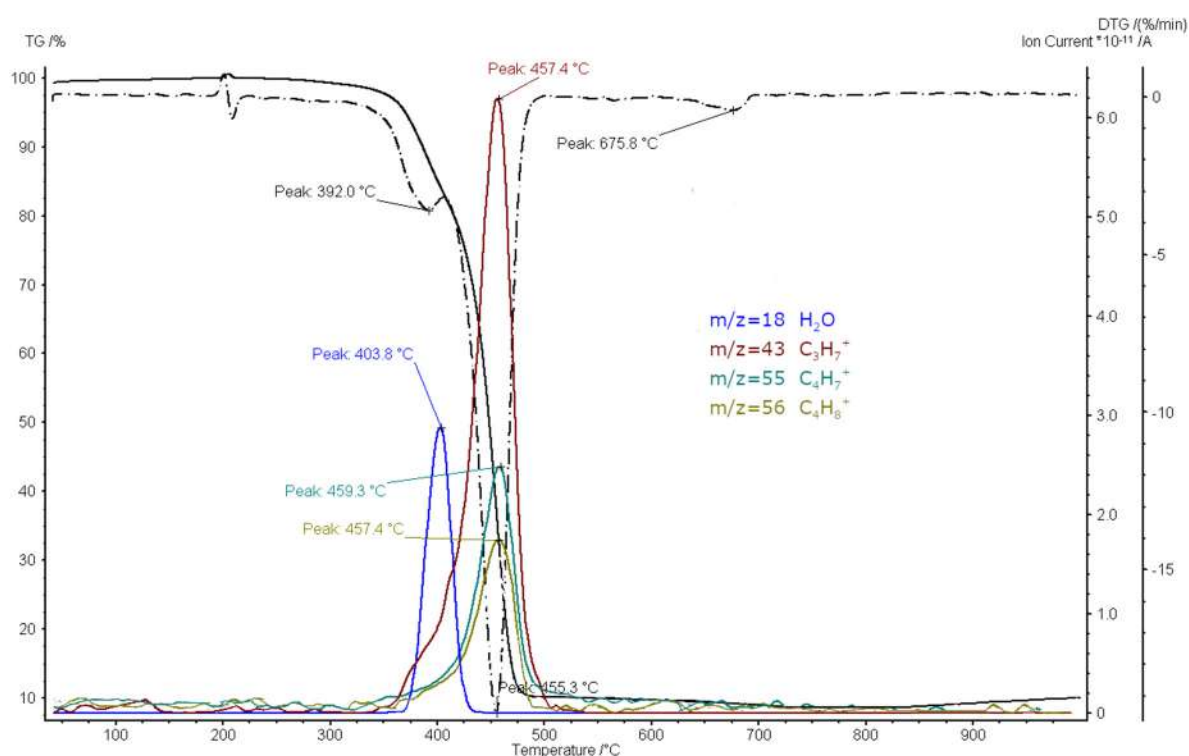


Figure 6. TG-DTG curves with curves of MS ion currents of volatile fraction (m/z 18, 43, 55, 56).

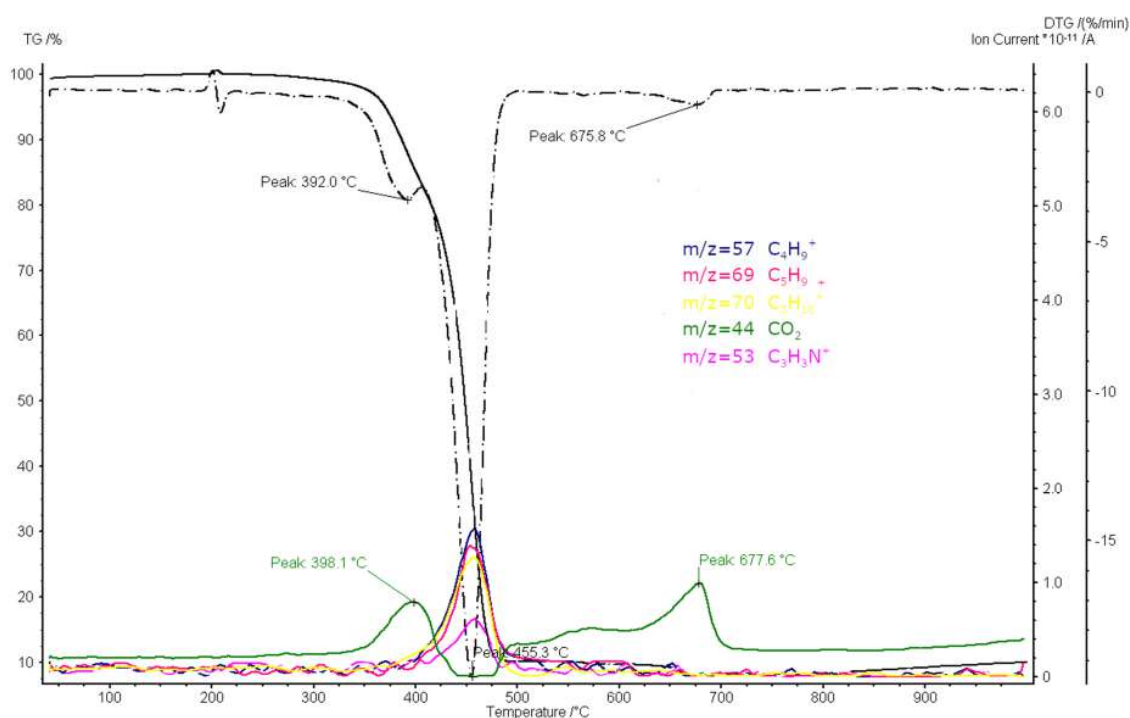


Figure 7. TG-DTG curves with curves of MS ion currents of volatile fraction (m/z 44, 53, 57, 69, 70).

3.4. Results of Computational Simulation

As part of the computer simulations, the effect of temperature was investigated on the proportion of primary pyrolysis gaseous products determining the calorific value of the pyrolysis gas—namely, CO, H₂, CH₄, C₃H₈, C₄H₄, C₆H₆, C₂H₂, C₂H₄, C₂H₆, and C₃H₆ (Figure 8).

The calculations show that the concentration of all the analysed compounds strongly depends on the process temperature. The largest share is observed for CO (up to 65%) in the entire temperature range but only for polyethylene terephthalate (PET). On the other hand, for PP and protective masks, a high proportion of hydrogen, even 50%, is visible, but only in the lower temperature range, i.e., from 400 °C to 500 °C. At the temperature of 700 °C, there is a clear decrease in the H₂ concentration to 15% for the masks and 22% for PP. At the same time, an increase in the hydrogen content from PET pyrolysis is observed; however, it does not exceed 5%. The opposite situation is observed for CH₄, the share of which increases with the rise in the process temperature, reaching a concentration of approx. 35% for both masks and PP at 700 °C, with a simultaneous low concentration (less than 5%) for PET. Noteworthy is the high proportion of C₆H₆ benzene in the pyrolysis gas for all the analysed wastes, at the level of approx. 20% for PP and masks and 17% for PET. From the energy point of view, the significant content of C₂H₄ is also significant, which grows with the temperature to approx. 9% at 800 °C for the masks and PP, and C₆H₆, reaching even 7% at the temperature of 650 °C for polypropylene. For the remaining compounds—namely, C₃H₈, C₄H₄, and C₂H₂ (except for PET), with increasing temperature, a sharp decrease in the concentration is observed for all the waste, and it does not exceed a 5% share in the pyrolysis gas.

The results of the model were compared with those of experimental research for RDF pyrolysis at 900 °C, presented in [47] (Figure 9).

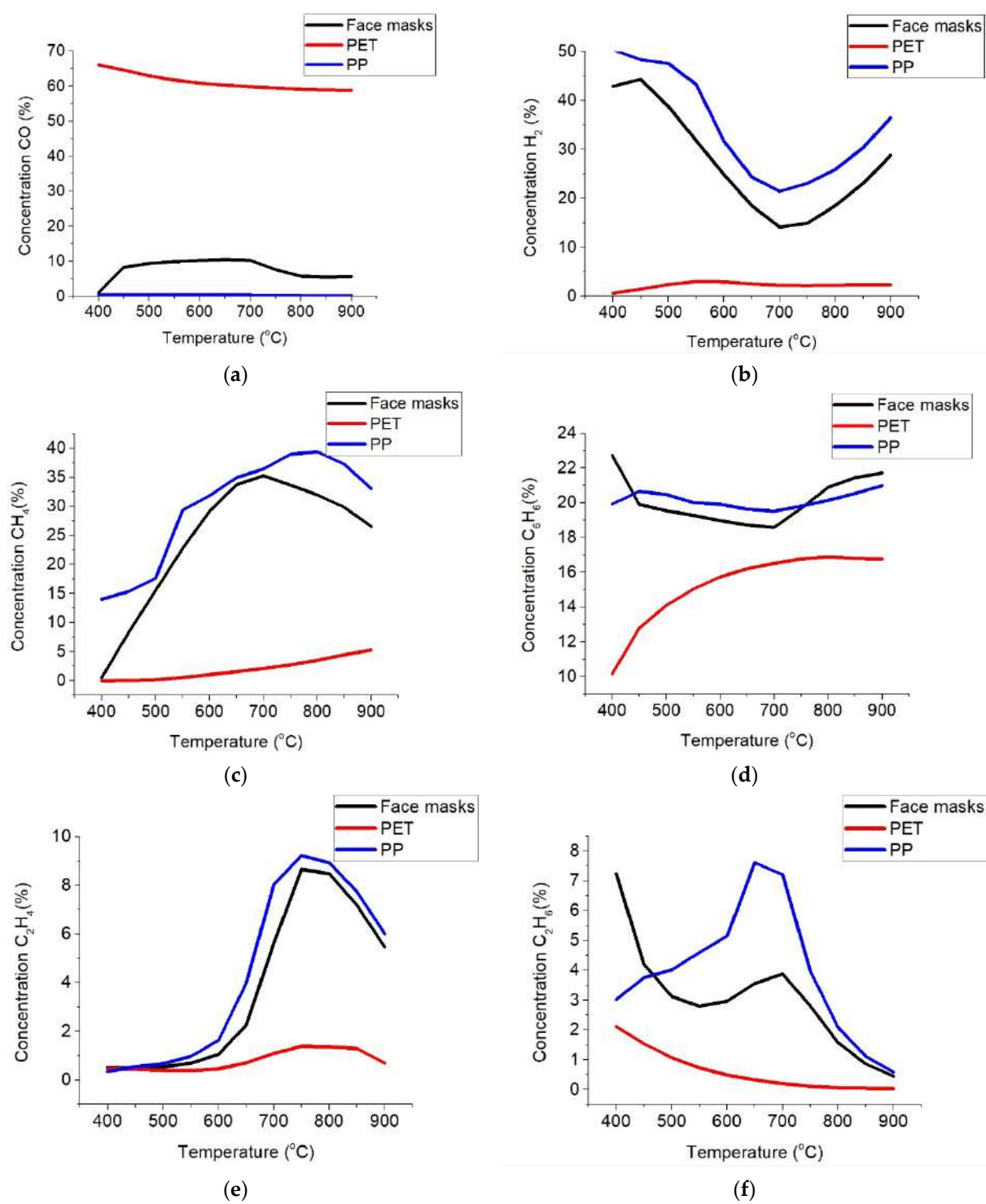


Figure 8. Cont.

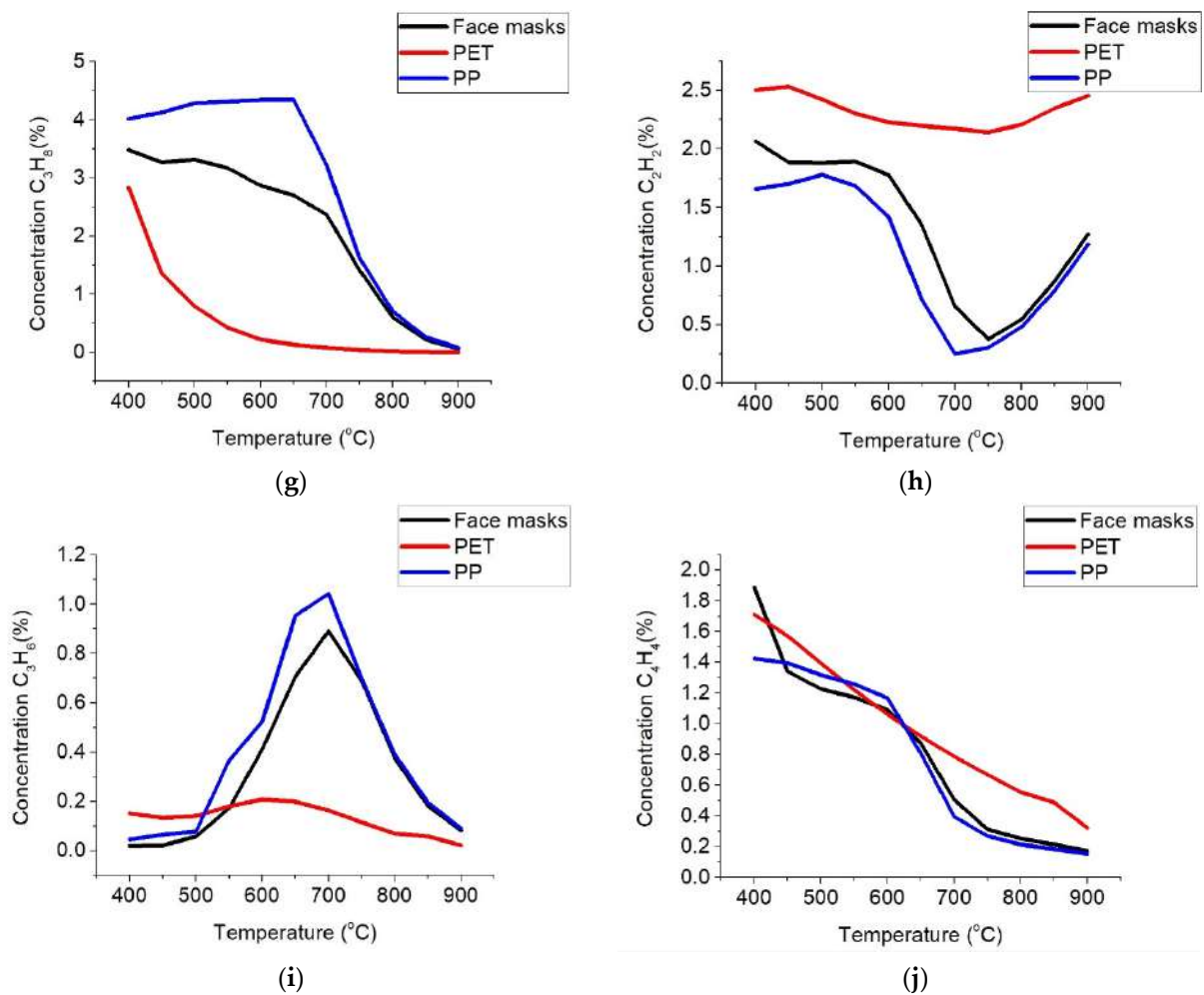


Figure 8. Influence of temperature on formation of (a) CO, (b) H₂, (c) CH₄, (d) C₆H₆, (e) C₂H₄, (f) C₂H₆, (g) C₃H₈, (h) C₂H₂, (i) C₃H₆, (j) C₄H₄.

Comparing the results obtained by modelling with the results from the experiment, the potential resulting from the pyrolysis of plastic waste, in particular polypropylene, the main component of protective masks, is visible. The high proportion of flammable compounds such as H₂, CH₄, and C₆H₆ translates into the high calorific value of the pyrolysis gas, amounting to 49.73 MJ/m³ for PP pyrolysis gas, and 47.74% for mask pyrolysis (Figure 10). It should be mentioned that the presence of heavy organic molecules and their derivatives in the wet pyrolysis gas, which can account for up to 30% of the gas volume, has a substantial impact on the high calorific value. As a result of the condensation of these chemicals, pyrolysis oil is produced. According to preliminary research undertaken by the article's authors, direct management of wet pyrolysis gas (i.e., a mixture of pyrolysis gas and gaseous oil) in high-temperature heating chambers with temperatures exceeding 1300 °C is possible. The disposal of the problematic liquid portion, i.e., pyrolysis oil, is favoured at such a high temperature, resulting in considerable economic gains. The proposed method is described in great detail in [62].

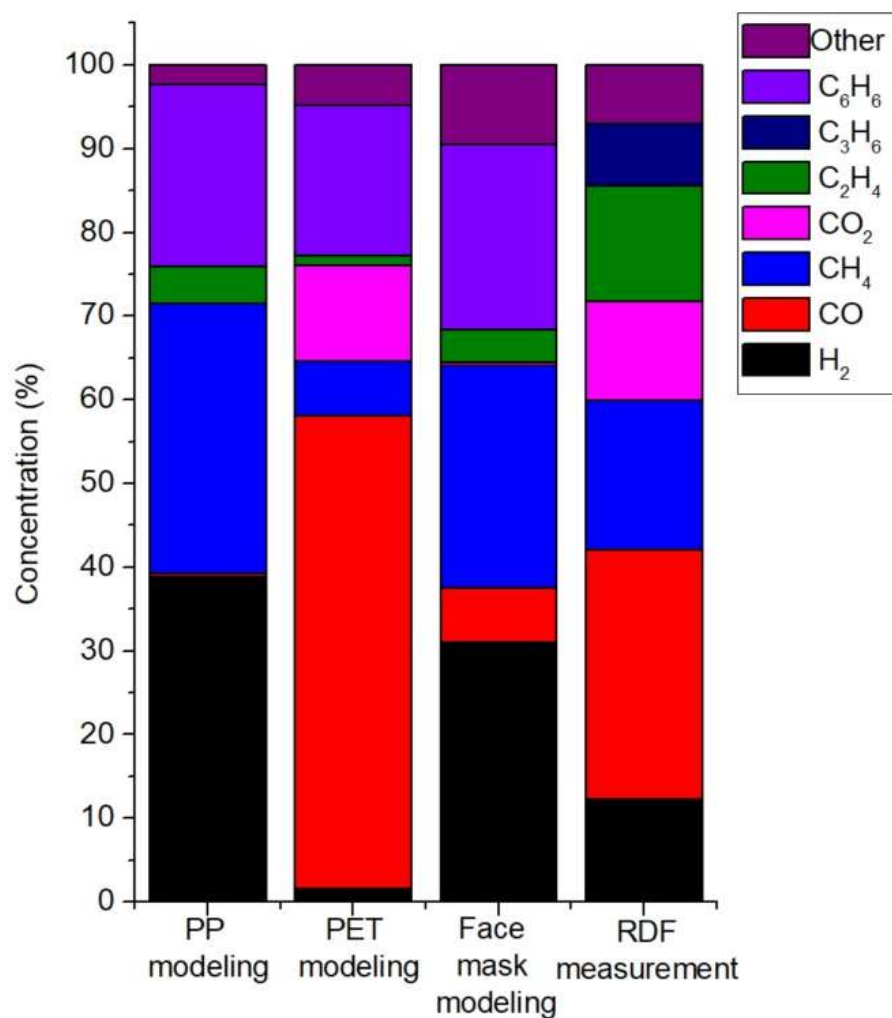


Figure 9. Comparison of selected gaseous pyrolysis products.

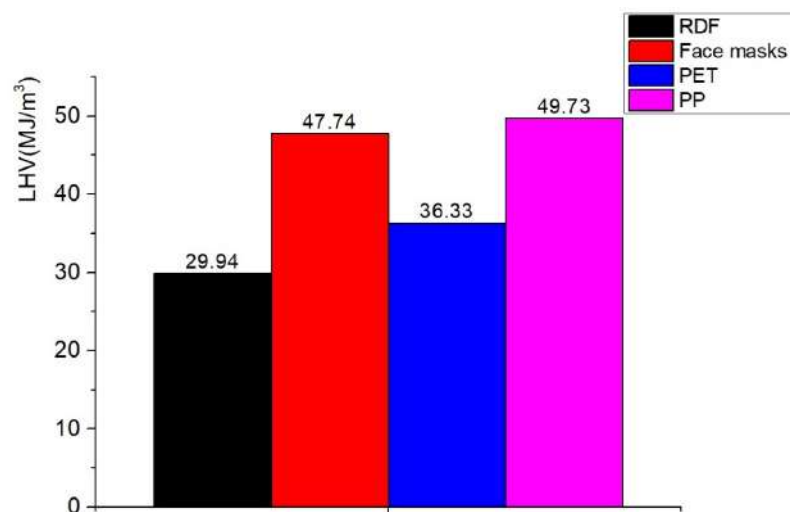


Figure 10. Calorific value of gas from pyrolysis of selected waste.

4. Conclusions

The following conclusions and statements were formulated based on the conducted research and the obtained results:

1. The pyrolysis of plastic waste generated during the COVID-19 pandemic is an effective and environmentally safe solution with great application potential.
2. Thermal conversion of waste by pyrolysis is characterized by a high yield of high-calorific pyrolysis gas. This gas can potentially be used as a substitute for natural gas for energy production.
3. It is possible to forecast the chemical composition of gaseous pyrolysis products of plastic waste and on this basis to estimate the calorific value of the pyrolysis gas produced in the process.
4. The pyrolysis of polypropylene, the main component of protective masks, allows one to obtain high-calorific pyrolysis gas (47.7 MJ/m^3), the main components of which are H_2 , CH_4 , and C_6H_6 .
5. The results of the conducted research and computer simulations show the enormous energy value of plastic waste, especially those generated during the COVID-19 pandemic. Increasing the share of the above-mentioned waste in the municipal waste stream from which the so-called overflow and RDF fraction will increase the calorific value of the pyrolysis gas.
6. Effective disposal of the new category of waste is both a technological- and material-related challenge. Solving this challenge and creating technological techniques and know-how will enable the safe treatment of municipal waste in the COVID-19 era, and will also point the way to effective thermal conversion products management.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en15072629/s1>. Figure S1 clarified the data of mass loss (TG) and maximum rate of mass loss (DTG) during the reaction, as well as the beginning and final temperatures at each step of the pyrolysis processes.

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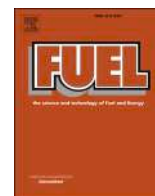
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Full Length Article

Numerical and experimental analysis of pyrolysis process of RDF containing a high percentage of plastic waste

Monika Zajemska^a, Aneta Magdziarz^{b,*}, Józef Iwaszko^a, Magdalena Skrzyniarz^a, Anna Poskart^c

^a Czestochowa University of Technology, Faculty of Production Engineering and Materials Technology, 19 Armii Krajowej Ave., 42-200 Czestochowa, Poland

^b AGH University of Science and Technology, 30 Mickiewicza Ave., 30-059 Krakow, Poland

^c Czestochowa University of Technology, Faculty of Management, 19 B Armii Krajowej Ave., 42-200 Czestochowa, Poland



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ABSTRACT

The current COVID-19 pandemic situation and the associated restrictions have increased the amount of generated waste. It results from the necessity to wear personal protective equipment. Thus, the disposal of masks and gloves is a topical issue and requires immediate investigation. The main aims of this work are management and environmental studies of municipal solid wastes (MSW), which have been generated during the COVID-19 pandemic time. Effective waste management in relation to a circular economy is presented. A sample of refuse derived fuel (RDF) with a high content of plastics was used for the experimental and calculation studies. Pyrolysis was selected as the best thermal decomposition process for this kind of wastes. Proximate and ultimate analyses were performed for RDF and its products. Pyrolysis was carried out using a pilot-scale reactor with a continuous flow of 250 kg/h at 900 °C. Thermogravimetric analysis was applied during the pyrolysis investigation and showed that the main decomposition of RDF took place in the temperature range of 250–500 °C. The pyrolysis gas contained combustible compounds like CO (19.8%), H₂ (13.2%), CH₄ (18.9%) and C₂H₄ (7.1%), giving a high calorific value – 24.4 MJ/m³. The experimental results were implemented for numerical calculations.

Chemkin-Pro software was applied to predict the chemical composition of the pyrolysis gas. The performed computer simulations demonstrated very good agreement with the results obtained during the experiments. They also indicated that there is a strong relationship between the chemical composition of the pyrolysis gas, the process temperature and residence time in the reactor.

1. Introduction

As indicated by the latest reports, the COVID-19 pandemic is a challenge not only from a medical and economic point of view, but also an environmental one, due to the enormous increase in the demand for personal protective equipment (e.g. surgical masks, protective gloves, gowns, goggles and disposable bags and foil gloves) and, as a consequence, an increase in the amount of generated medical waste [1]. The record waste growth of 370% was reported in Hubei Province in China [2]. Fearing the spread of the virus, some countries, such as the US, have partially stopped recycling programs, while restoring the widespread use of single-use plastic bags [3]. Moreover, pandemic restrictions (closed restaurants) have led to an increase in the amount of plastic packaging waste from food delivery and takeaway [4]. The greatest

threat is posed by medical waste from quarantined persons from households, which is not subject to restrictive storage and disposal procedures [5]. This waste is most often disposed of as mixed waste in municipal landfills, posing a huge threat to the natural environment and human life [6]. Taking into account all these facts, effective management and disposal of the above-mentioned waste is a global challenge, forcing a review of the technologies and solutions used so far, enabling their safe and effective management [7]. The development of municipal waste management services, especially in urban areas, is not able to keep up with the fast pace of urbanization despite numerous initiatives taken by governments [8]. In addition, the rising costs of disposal, which, according to Aleluia and others, may account for as much as 50% of the city authorities' budget [9] do not favour proper waste management. Furthermore, more and more stringent regulations in European

* Corresponding author.

E-mail address: amagdzia@agh.edu.pl (A. Magdziarz).

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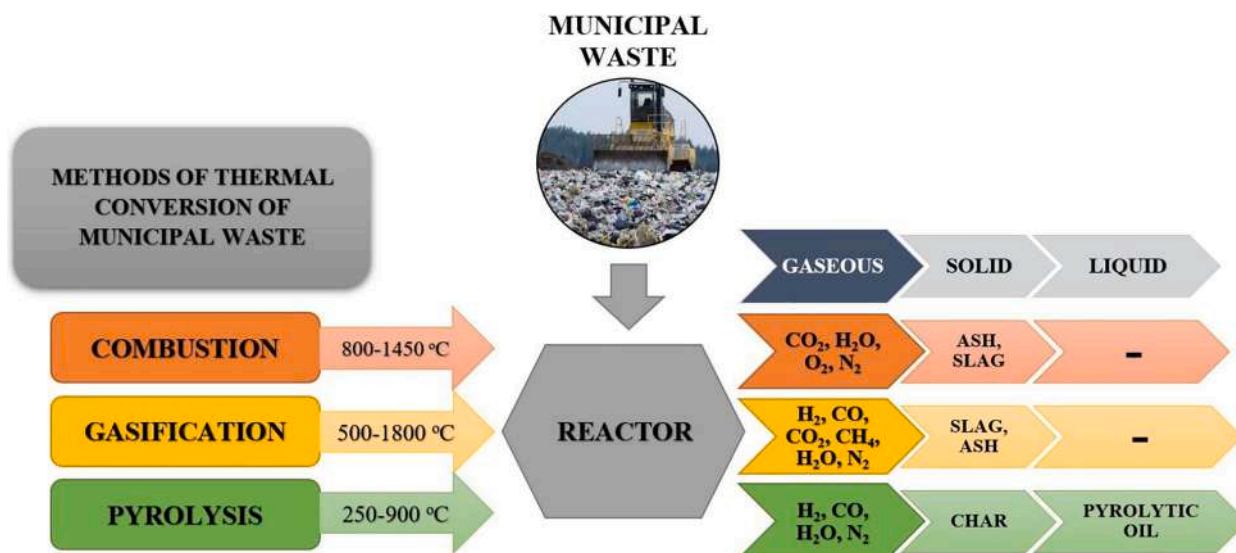


Fig. 1. Thermal waste conversion methods [14].

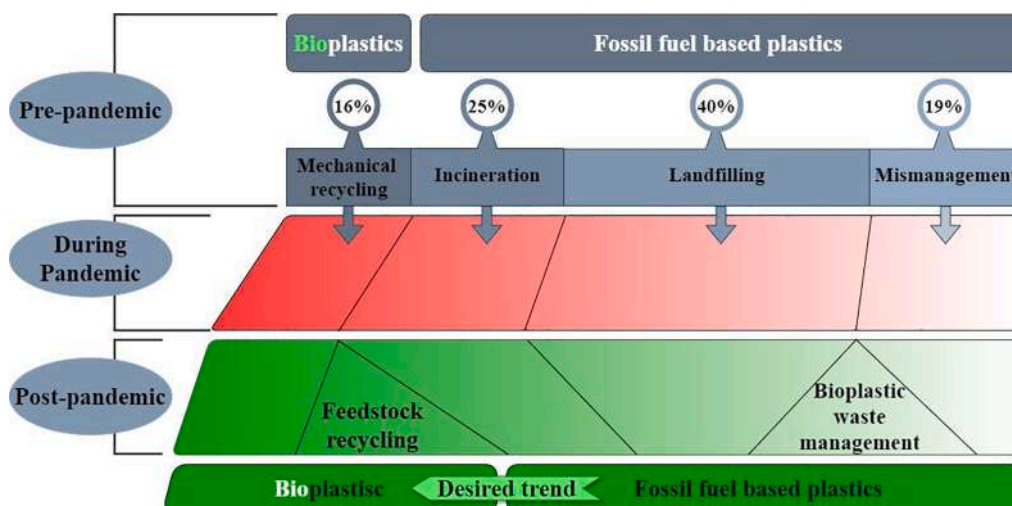


Fig. 2. Plastic waste generation trends and COVID-19 implications for existing waste management systems and likely solutions to challenges in post-pandemic waste management systems [7].

legislation, aimed at reducing the environmental burden associated with the storage of MSW [10] determine the directions of waste management, i.e. material (recycling) [11] and energy recoveries using thermal waste conversion methods (combustion, gasification, pyrolysis) (Fig. 1) [12,13].

Pyrolysis and gasification allow the recovery of chemical energy in the form of secondary fuels or provide raw materials for other processes [15], while incineration enables the recovery of electricity and heat [16]. As indicated by the research conducted by Wang et al. [17], undesirable by-products resulting from waste conversion may also be a valuable carbon material at the nanoscale. An example is soot from the high-temperature thermal-chemical conversion of plastic waste. The most common technology of thermal conversion of RDF in Poland is its incineration, while in the face of the constant reduction of pollutant emissions in European legislation, other, more environmentally friendly methods of managing alternative fuels from waste are sought. It seems that the improvement of the overall energy recovery from waste, by combining the efficiency of installations currently operating in Poland, using rotary kilns of cement plants and new pyrolysis and gasification installations, e.g. located in mechanical-biological waste treatment

(MBT) plants, will allow for further reduction of the role of landfilling in the Polish waste management. Firstly, it will ensure compliance with the increasingly demanding European regulations [18], and secondly, it will contribute to the rational use of natural resources, while increasing the level of environmental protection [19].

The large-scale implementation of plants for energy recovery from waste may allow in the long term reduce the independence on fossil fuel import. Average estimates suggest that each ton of chemical municipal waste replaces 0.4 tonnes of coal used to generate electricity in the US per year [20]. As indicated by numerous literature sources, one of the most beneficial strategies for municipal solid waste management (MSWM) is the conversion of waste into Refuse Derived Fuel (RDF) [21,22]. RDF can be used as a substitute for conventional fossil fuel in the cement industry [23] and for electricity generation [24]. The efficiency of the methods of thermal processing of MSW is varied, which results from the variable morphology of waste, depending on e.g. from the place of their occurrence [25]. Due to the high flexibility of the obtained products [26], lower emission of pollutants into the air, e.g. SO₂ and NO_x, compared to incineration and better quality of the solid residue, the pyrolysis process deserves attention [27]. Pyrolysis is a

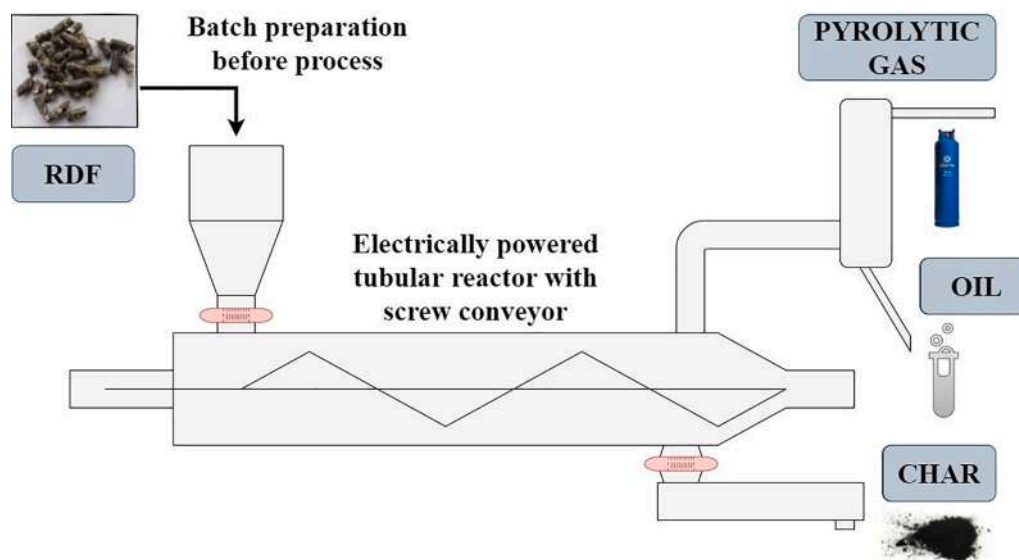


Fig. 3. Diagram of installation for conducting the RDF pyrolysis process.

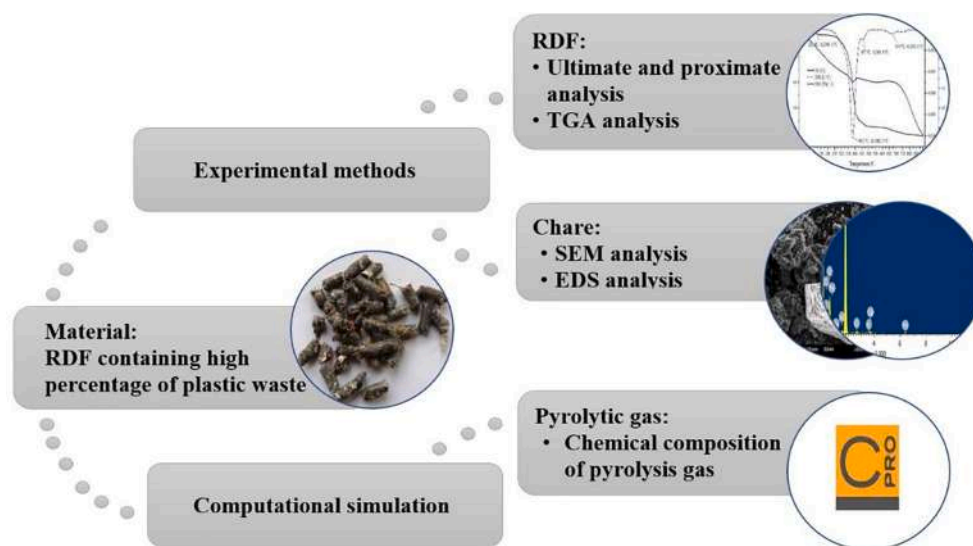


Fig. 4. Research scheme.

thermochemical process carried out without oxygen, resulting in the formation of three main products [28], namely: solid (solid residue rich in carbon (char)) [29], liquid fraction (from the condensation of released volatile matter (pyrolysis oil)), and gaseous (including CO, CO₂, CH₄, and H₂), suitable for direct use [30]. The share and quality of products depend on type of waste, pellet packing density, process temperature, type of reactor, residence time and heating rate [31,32]. Most often, RDF undergoes the pyrolysis process at a temperature of 400–900 °C [33] and depending on the set parameters of the process, variable proportions of the obtained products are obtained [34]. Noteworthy is the high calorific value of gas from the pyrolysis of RDF fuel, ranging from 15 to 30 MJ/m³ [35], encouraging its use for energy purposes [36,37].

1.1. Management of waste

The COVID-19 pandemic had a negative impact not only on the global economy, but also on the efficient functioning of local governments and the proper management of municipal waste [38].

Municipalities and cities around the world are struggling with increased amounts of solid waste and medical waste, with less budget inflows due to the economic slowdown [39]. Insufficient forces and resources at the disposal of local governments make them unable to deal with the growing amount of hazardous waste deposited in municipal landfills [40]. The material specificity of this waste significantly differs from the composition of typical municipal waste, due to the presence of a considerable amount of medical waste and an above-average amount of plastic waste [41]. Therefore, the currently operating waste management systems based on landfilling, due to the negative impact on the environment and people, should be replaced with innovative solutions based on thermal neutralization [42]. At present, incineration is the most frequently used method of thermal conversion of municipal solid waste [43]. Other methods of thermal conversion (pyrolysis, gasification) are still in the research phase and they meet with some problems in large scale implementation in Poland [44]. The reasons for the above-mentioned situation can be seen in the lack of sufficient data characterizing municipal waste, poor quality of the raw material, or inadequate structure of the facility [45,46].

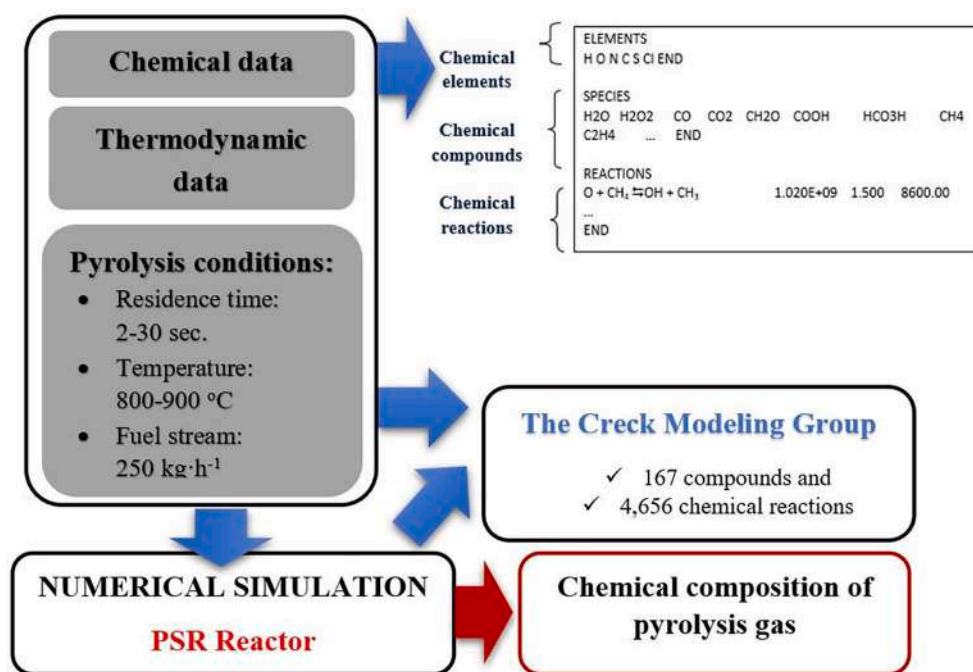


Fig. 5. Modelling procedure diagram.

Table 1

Proximate and ultimate analysis of RDF, solid residue (char) and oil samples obtained from RDF pyrolysis below 900 °C.

Type of sample	RDF	Solid residue (char)	Oil
Sample view			
C, %	50.73	20.04	62.11
H, %	6.19	0.98	31.94
N, %	0.71	0.34	1.04
O, % (bal.)	42.37	78.64	4.91
Calorific value, MJ/kg	20.47	10.82	35.01

The analysis carried out by Vanapalli et al. [2,7] shows that the most widely used techniques for the management of plastic waste are mechanical recycling, incineration and landfilling. At the same time, the authors point out that these techniques are far from perfect in tackling the entire problem of plastic waste. In addition, the development of new solutions should be intensified all the more in connection with the increased amount of waste generated during the COVID-19 pandemic. Trends in plastic waste generation and consequences of pandemic for existing waste management systems and likely solutions to challenges in post-covid-19 waste management systems are shown in Fig. 2 [2,7].

The motivation to undertake research within the above-mentioned issues was the dynamic growth of global interest in the pyrolysis of waste, especially plastics, as well as the current situation on the waste market in Poland and the related problem of the effective management of waste generated during the pandemic. It is worth noting that pyrolysis is a very complex process in terms of chemistry; hence, the possibility of predicting the physical and chemical properties of pyrolysis products

requires systematic experimental and numerical tests. An additional argument supporting the above-mentioned issues is fact that there are not many studies concerning chemical composition of gaseous products of waste pyrolysis, in particular plastic waste based on experimental and numerical investigations. The results of computer calculations presented in this paper complement the current one and provide new knowledge on the chemical mechanisms of the formation of gaseous products of waste pyrolysis process. Moreover, the use of a computational tool such as the ANSYS CHEMKIN-PRO software, which enables a detailed analysis of the chemical composition of gaseous pyrolysis products, is innovative.

The study investigated RDF with a high proportion of plastics as the raw material in the production of potentially valuable products obtained by pyrolysis. Detailed and extensive instrumental analyses of the pyrolysis products were carried out. The obtained results proved the usefulness of employing computer simulations to forecast the gaseous products of thermal conversion.

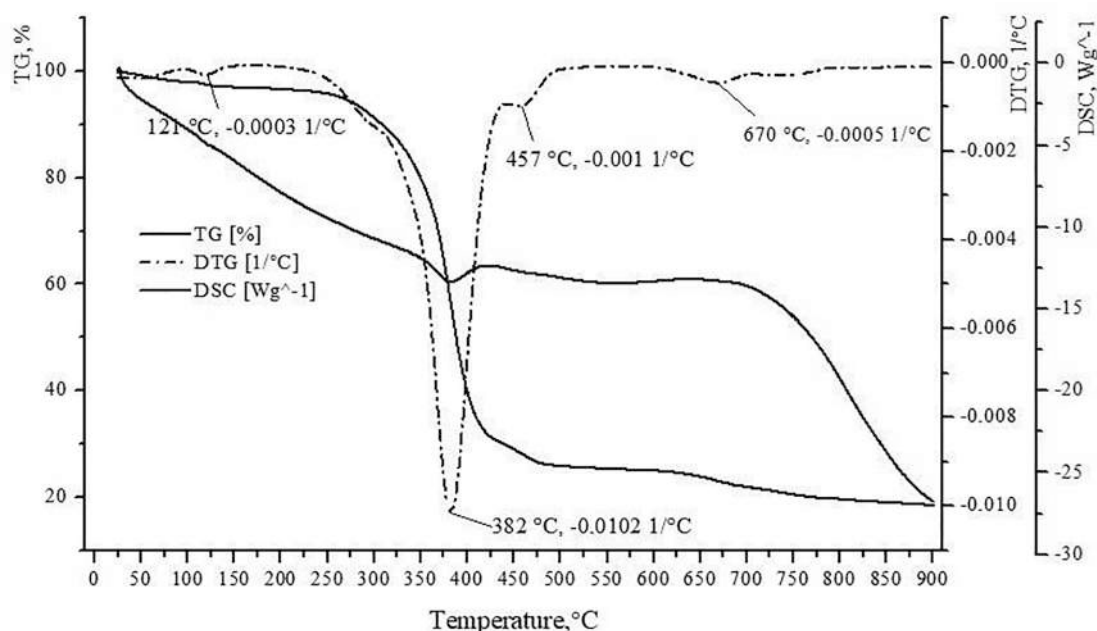


Fig. 6. TG, DSC and DTG curves during RDF pyrolysis in nitrogen atmosphere.

2. Materials and methods

2.1. RDF sample

Samples of RDF pellets and pyrolysis products, i.e. pyrolysis oil and char, used for the tests, came from the Polish Waste Management Plant. The input material, in the form of an over-sieve fraction of municipal waste, from which RDF pellets were made with the dimensions 2 cm in length and 6 mm in diameter, contained 60% plastic waste, including waste generated during the pandemic (e.g. gloves and protective masks) in addition to paper, cardboard and foil. The pyrolysis process was carried out under oxygen-free atmosphere at 900 °C.

Owing to the energy efficiency (i.e. the percentage of energy contained in the mass unit of the obtained pyrolysis product in relation to the energy contained in the mass unit of the feedstock) of the obtained pyrolysis products (80% pyrolysis gas, 15% char, 5% pyrolysis oil), the pyrolysis gas and char were subjected to detailed analysis.

2.2. Pyrolysis reactor scheme

The pyrolysis process was carried out using a pilot pyrolysis Auger reactor with a continuous flow of 250 kg/h at 900 °C. The reactor was equipped with an electrically heated spiral heating coil that also acted as a conveyor along the axis of the reactor. A schematic diagram of the process is shown in Fig. 3.

Due to the residence time of the batch in the reactor, i.e. about 20–25 min, the process is classified as an intermediate process, between slow pyrolysis used in batch reactors (4 h) and fast pyrolysis in fluidized bed reactors (~1 s) [47]. The pressure in the reactor was close to atmospheric or slightly under pressure. The raw hot gas left the reactor and went to a vertical and insulated gravity settling tank, enabling the initial separation of dust from the raw gas. The process gas from pyrolysis flowed through the pipeline to the modular shell-and-tube recuperator. Process air was fed in counter-flow through the shell, which was heated to a temperature of 200 °C, was directed to the gas launcher or was used in the process of drying waste. Cooled process gas with a temperature of approx. 550 °C fed the dedusting and desalting system. The gas then went to a system of two shell and tube coolers (condensers), where a condensing liquid fraction and gas at a temperature below 20 °C were formed. When the gas was cooled, residual water

and organic condensate (mainly BTEX and naphthalenes) condensed. Additionally, the condensed liquid was collected in the condensate separator. Then the gas was sent to the last stage of purification, which was a series of two filters with an input of active carbon in the form of pellets and other additional sorbents to absorb residual impurities of tar substances, sulphur compounds, chlorine, siloxanes and others. Additional sorbents to absorb impurities were mineral sorbents in the form of granules with an absorbency of up to 120%. The adsorption mechanism made it possible to keep the guaranteed concentrations, especially of naphthalene and derivatives, and thus ensure the safe operation of the incineration generator [48]. All condensates, liquids or suspensions were collected by gravity through runoff to pallet containers [49]. The composition of the pyrolysis gas was analyzed by gas chromatography. The scope of the conducted studies and research is presented schematically in Fig. 4.

2.3. Proximate and ultimate analysis

The elemental analysis of the studied materials was performed by means of a LECO CHN628 elemental analyser. The carbon (C) hydrogen (H) and nitrogen (N) contents were determined. Determination of the elements is based on the combustion of a sample under pure oxygen at 950 °C. Helium carrier gas sweeps the combustion gas to separate infrared cells utilized for the detection of H₂O and CO₂, while a thermal conductivity cell is used to detect nitrogen. The oxygen (O) content was calculated by difference.

2.4. TGA

Thermal analysis was performed to study the thermal behaviour. The sample was subjected to a temperature program (heating rate – 10 K/min) in order to measure the pyrolysis process (atmosphere – nitrogen, flow rate – 40 mL/min). As the output, TGA and DSC curves were obtained. TGA reflects the change in mass of a sample as a function of temperature. The TGA curve was used to detect changes in the sample mass. The DSC signal is the energy absorbed by or released by the sample. The DSC curve enables the detection of endothermic or exothermic effects, and temperatures that characterise a peak. DTG is the first derivative of TGA.

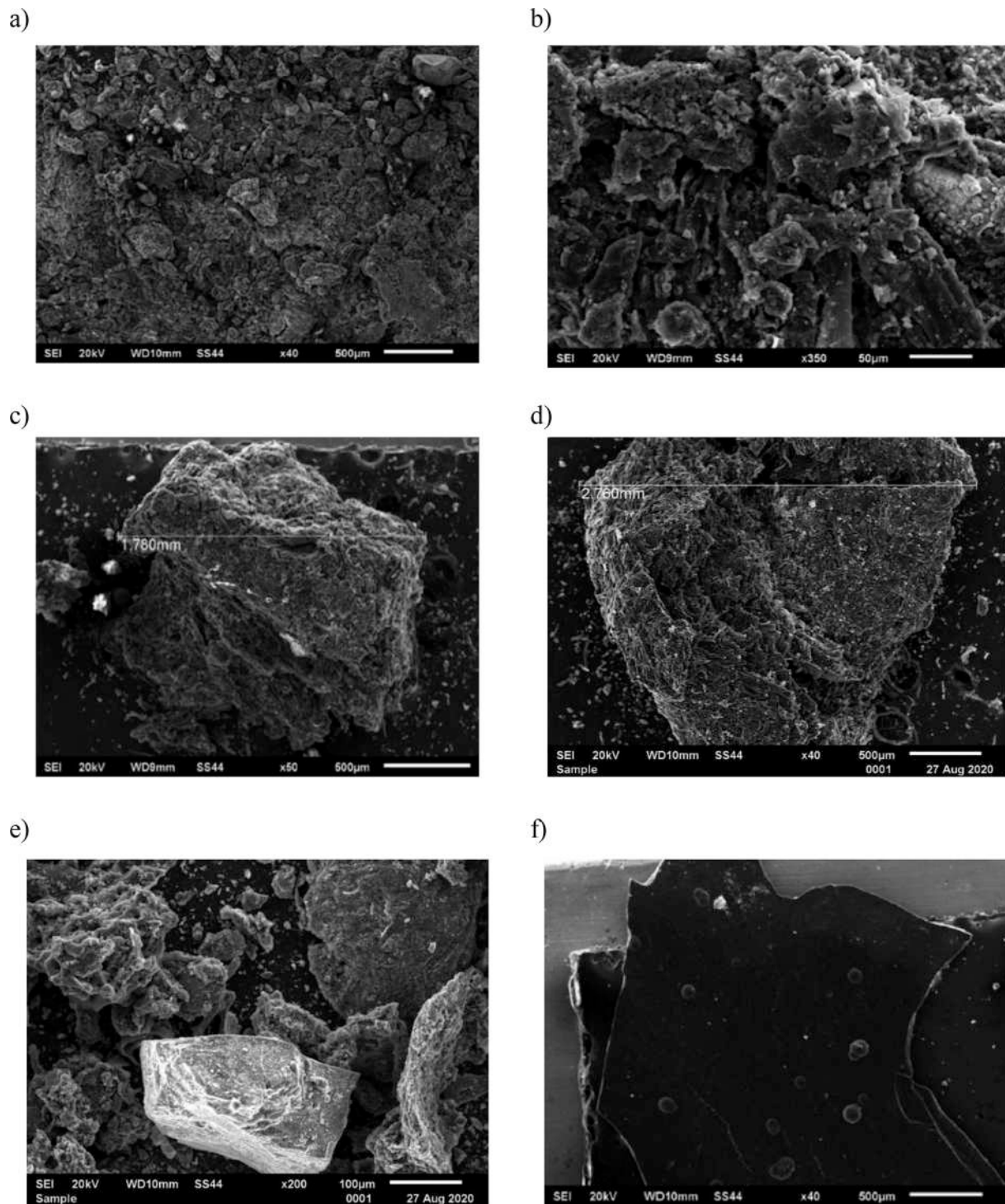


Fig. 7. Microstructure of dominant fraction (a, b), microstructure of particles larger than 1 mm (c, d), microstructure of particles with polyhedral shape (e), microstructure of flat particles with low degree of surface development (f).

2.5. SEM and EDS analysis

Microstructure examinations were performed for the char sample by means of a JEOL JSM-6610LV scanning electron microscope. In order to obtain the most complete microstructural characteristics of the char, both places representative of the analysed sample and areas showing a different microstructure and morphology were examined. Additionally, in the case of particles with a distinctly different microstructure and morphology from the fraction dominating in the char, EDS studies were carried out to identify their chemical composition and, consequently, to

identify the type of waste that was the source of these particles. The EDS examinations were conducted using an X-ray microanalyzer by Oxford Instruments working with the JEOL JSM-6610LV scanning microscope.

2.6. Numerical method

Calculations were made based on experimental (process) data. The methodology is described in papers [32,35] and there was used licensed Ansys Chemkin-Pro software [50–53]. The data was applied for the calculations: i) 2–30 s residence time in highest temperatures zone; ii)

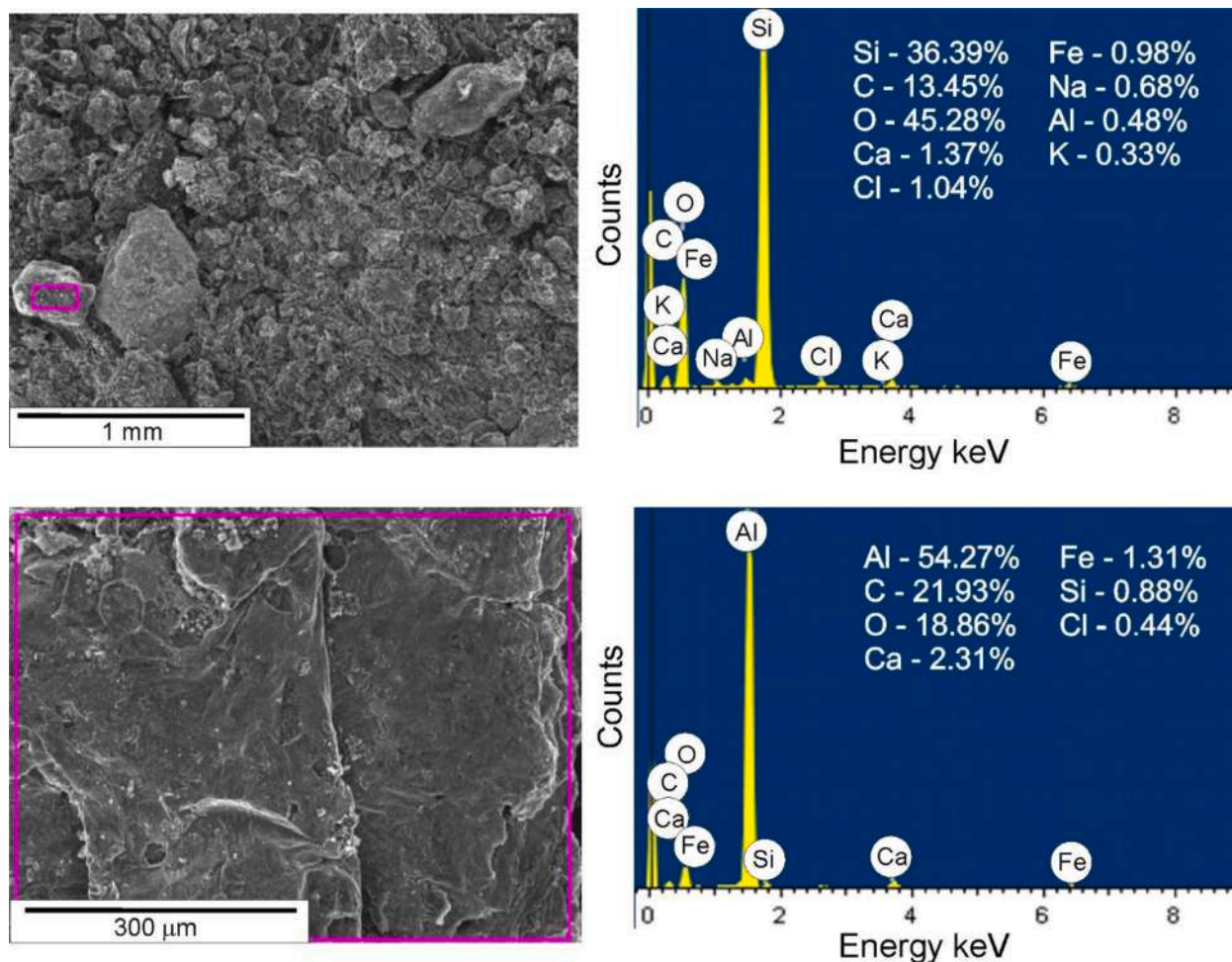


Fig. 8. Results of EDS analysis.

Table 2

Pyrolysis gas composition from RDF pellet pyrolysis tests.

Chemical compound	Test 1	Test 2	Test 3	Test 4	Test 5	Average value	Unit
CH ₄	18.9	22.9	20.4	24.6	24.3	22.22	%
H ₂	13.2	18.5	16.4	22.8	21.3	18.44	%
CO	19.8	12.6	19.6	23.6	23.1	19.74	%
CO ₂	21.1	14.8	16.2	17.5	16.2	17.16	%
C ₂ H ₄	7.1	10.9	13.0	5.4	6.8	8.64	%
C ₂ H ₆	2.3	1.3	1.9	0.7	0.9	1.42	%
C ₃ H ₈	6.1	1.5	2.9	0.5	0.9	2.38	%
C ₄ H ₁₀	3.7	0.7	0	0.2	0.4	1.0	%
O ₂	1.4	3.8	2.4	1.2	1.4	2.04	%
N ₂	6.9	13.1	7.1	3.5	4.7	7.06	%
HHV	26.5	21.5	23.4	19.0	20.0	22.08	MJ/m ³
LHV	24.4	19.7	21.5	17.3	18.4	20.26	MJ/m ³

800–900 °C temperature range; 250 kg·h⁻¹ fuel stream. The range of temperature was done based on TGA results, which showed that no significant changes took place above the temperature of 800 °C.

A detailed chemical mechanism developed by The Creck Modeling Group, involving 167 compounds and 4,656 chemical reactions, was implemented for the calculations. The mechanism took into account the detailed mechanism of high-temperature chemistry of HCl and Cl₂ presented in [54].

A diagram of the modeling procedure is shown in Fig. 5.

3. Results and discussion

3.1. Experimental results

3.1.1. Elemental analysis

In Table 1 the elemental analysis as well as calorific values of the studied RDF, obtained char and oil are presented. The studied RDF was typical with contents c.a. 50% carbon and 6% hydrogen and a calorific value of 20 MJ/kg. Such properties allowed successful pyrolysis to obtain high-quality pyrolysis oil and gas. The solid residue can find applications as well.

Fig. 6 presents the TGA, DSC and DTG curves of the pyrolysis process of the studied RDF sample. The first noticeable DTG peak and mass loss reflect the moisture content release (up to c.a. 200 °C). Next, based on TG, one main mass loss is observed in the temperature range from 200 to 425 °C, with the maximum DTG peak at 382 °C. At this stage, the endothermic DSC be assume that main decomposition takes place is detected. This stage is mainly related to the degradation of plastic components, as well as cellulosic components. It can be stated that the main decomposition takes place at a high rate. Additionally, two small peaks on the DTG curve are detected at 457 and 669 °C, respectively. They can be connected with the decomposition of more thermally stable plastic components (LDPE) or lignin [55]. The peak above 700 °C was found for cotton by [55]. Above 750 °C a slight change in the mass is observed. Similar tendency was detected in RDF studied by others [56,57]. Also Sipra A.T. et al. [58] reported that above 500 °C some peaks can appear during RDF decomposition under N₂ and CO₂. At 900 °C solid residue was 20% of the initial mass of the sample.

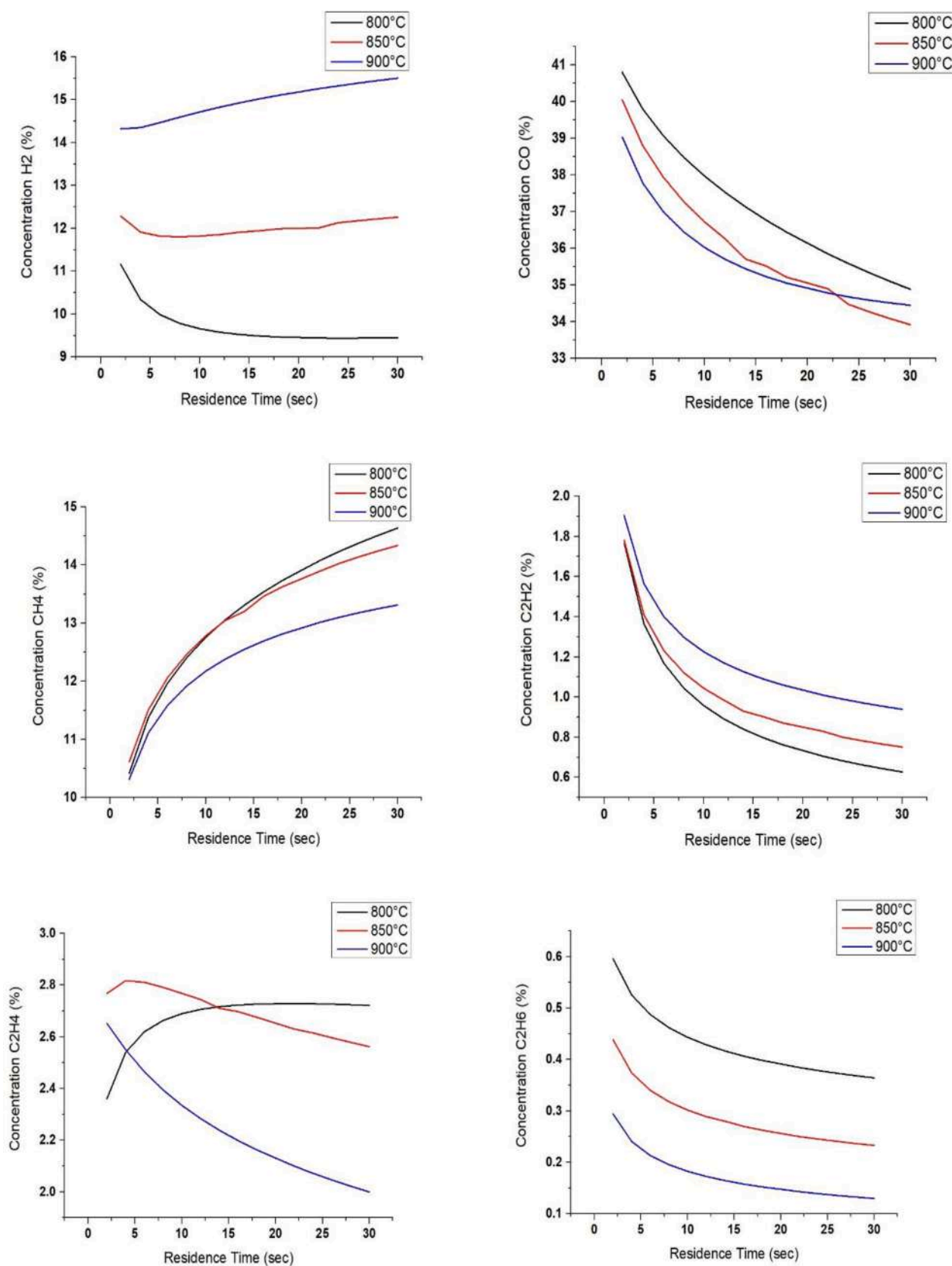


Fig. 9. Effect of residence time on concentration of selected gaseous pyrolysis products.

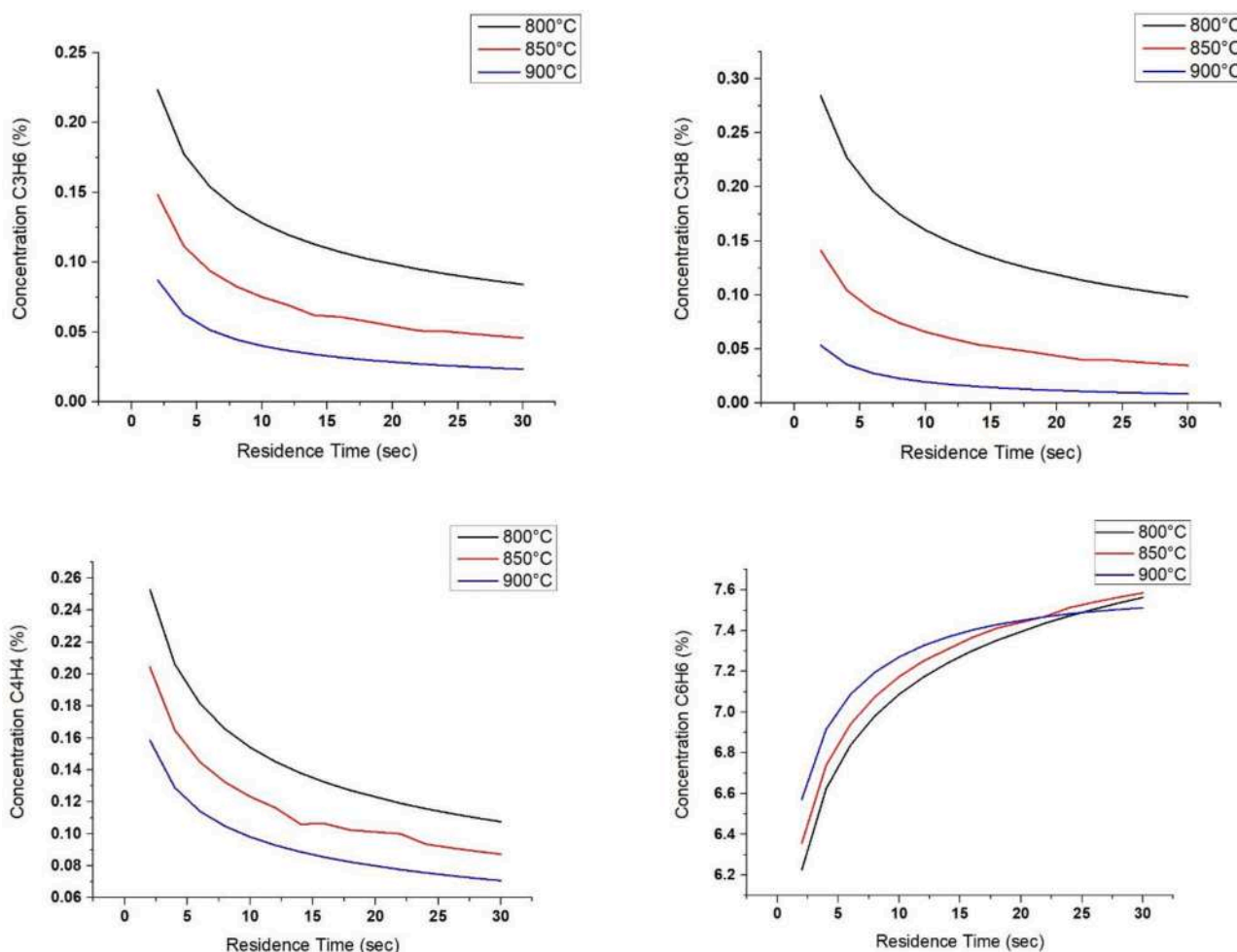


Fig. 9. (continued).

3.2. Pyrolysis solid products – Char analysis

3.2.1. SEM analysis

SEM investigations of the solid residue (char) revealed strong differentiation of the material both in terms of morphology as well as the size of the particles present in it (Fig. 7 a-f). Particles ranging in size from tenths of a micrometre to a few millimetres were present in the char, with the dominant fraction being 10 µm to 200 µm. These particles were characterized by an irregular shape and a high degree of surface topography. On the other hand, particles with dimensions above 1 mm were less numerous (Fig. 7 c,d). These particles were characterized by similar morphological features and surface topography as the dominant fraction; therefore, it should be assumed that at least some of these particles could have arisen as a result of the mechanical connection (interlocking) of smaller particles during movement of the char in the furnace space, as well as after the completion of pyrolysis, for example in during the dumping operation. Considering the extensive geometric structure of the surface and the irregular shape of the particles, such a situation was considered very likely. Moreover, there were not many flake-like particles in the char, characterized by a lower degree of surface development, and probably a residue of the starting material with a similar morphology, which did not decompose during thermal treatment, thus maintaining its original shape and microstructure (Fig. 7f). Additionally, numerous particles of a regular, polyhedral shape and more compact structure than the dominant fraction were found (Fig. 7e). In general, the degree of development of the surface of the char components was very diverse, which can be explained by the diversity of

the material subjected to thermal conversion and the different chemical compositions of the individual components of the analysed specimen.

In the case of particles whose shape or surface topography were clearly different from the dominant fraction, EDS chemical composition was conducted in order to identify the type of waste that was their source. Based on the performed EDS analyses, it was found that SiO₂ silica particles and aluminium waste were present in the char. An example of the EDS analysis of the SiO₂ particles is shown in Fig. 8a, and of the aluminium waste in Fig. 8b. The analysed area is marked with a frame. Compared to the dominant fraction, the silica particles are characterized by a clearly smaller specific surface and mostly regular polyhedral shape. In turn, the aluminium waste is in the form of flat particles with a small thickness and a small specific surface. The aluminium waste present in the char is most likely a residue of multi-material waste containing aluminium in the form of thin layers or foils.

3.3. Pyrolysis gas products from pilot installation

The results of the analysis of the gas composition from RDF pyrolysis from the pilot plant are summarized in Table 2. Due to the heterogeneous nature of RDF, this table lists 5 measurements, carried out for the same process conditions, i.e. the temperature of 900 °C in an oxygen-free atmosphere.

Measurements were carried out at time intervals for the same process conditions and the same batch material. The differences in the gas composition are the result of the different morphology of the municipal waste from which the pellets were made.

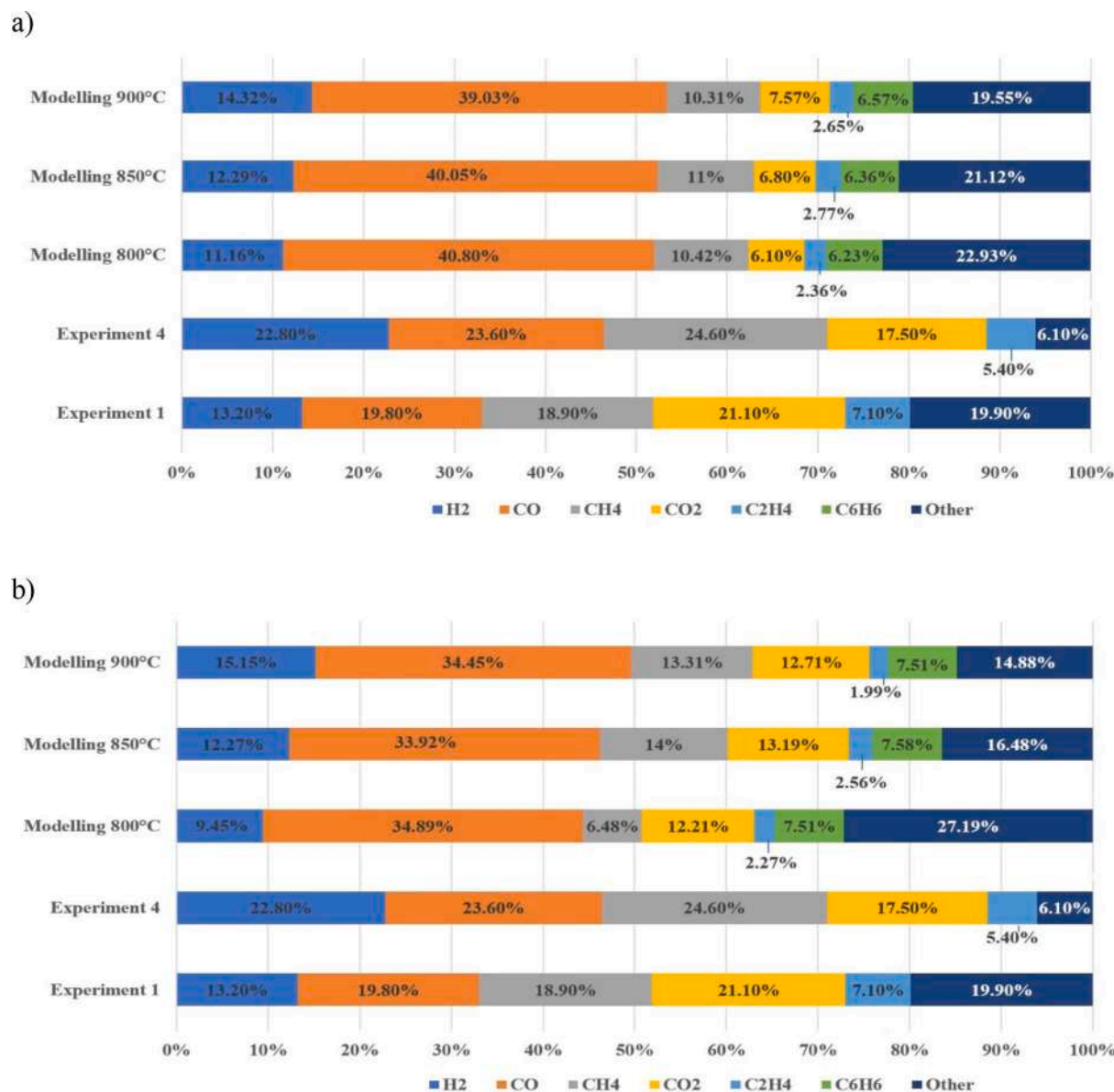


Fig. 10. Comparison of calculated and experiment results for selected concentrations gaseous pyrolysis products: a) residence time 2 s; b) residence time 30 s.

3.4. Calculation results

3.4.1. Numerical calculations of pyrolysis gas products

As part of the computer simulations, the detailed chemical composition of the pyrolysis gas was determined for the process conditions, and the influence of the temperature and residence time in the reactor in the zone of the highest temperatures on the share of the main gaseous products of pyrolysis determining the calorific value of the pyrolysis gas was analysed, namely CO, H₂, CH₄, C₃H₈, C₄H₄, C₆H₆, C₂H₂, C₂H₄, C₂H₆ and C₃H₆ (Fig. 9).

The calculations show that the concentrations of all the analysed compounds strongly depend on the residence time in the highest temperatures zone. A shorter residence time, i.e. less than 5 s leads to a higher concentration of most of the analysed compounds, i.e. CO, H₂, C₂H₂, C₂H₆, C₂H₄ (except for the temperature of 800 °C), C₃H₆, C₃H₈ and C₄H₄ for the three pyrolysis temperatures. The concentrations of the above-mentioned compounds decline with an increasing residence time. The opposite situation is observed for the remaining compounds, i.e. CH₄ and C₆H₆, the proportions of which increase with an increasing residence time. The largest share of the combustible compound in the

pyrolysis gas is observed for CO for the entire analysed range of residence time, with the highest concentration at the temperature of 900 °C and amounts to 40.08%. There are also significant proportions of hydrogen and methane in the pyrolysis gas. The highest concentration of hydrogen was recorded for 900 °C, i.e. 15.3% within 30 s, while methane for the longest time at 800 °C was 14.5%. Noteworthy is the high share of C₆H₆ at the level of 7.5%, which was not determined in the experimental conditions. The share of the other compounds for the analysed residence time and temperatures did not exceed 3%.

The obtained modelling results were compared with the results of experimental studies obtained from RDF pyrolysis carried out at the temperature of 900 °C (Fig. 10). The maximum and minimum analysed values of the residence time in the reactor, i.e. 2 and 30 s, were taken into account.

Comparing the results obtained by modelling with the results from the experiment, good agreement is observed as evidenced by the high proportion of flammable compounds such as CO, H₂, CH₄ and C₂H₄, for all the analysed cases. The modelling results clearly indicate a high proportion of benzene in the pyrolysis gas in the range of 6.23–7.58%. It should be emphasized that in the experiment the concentrations of

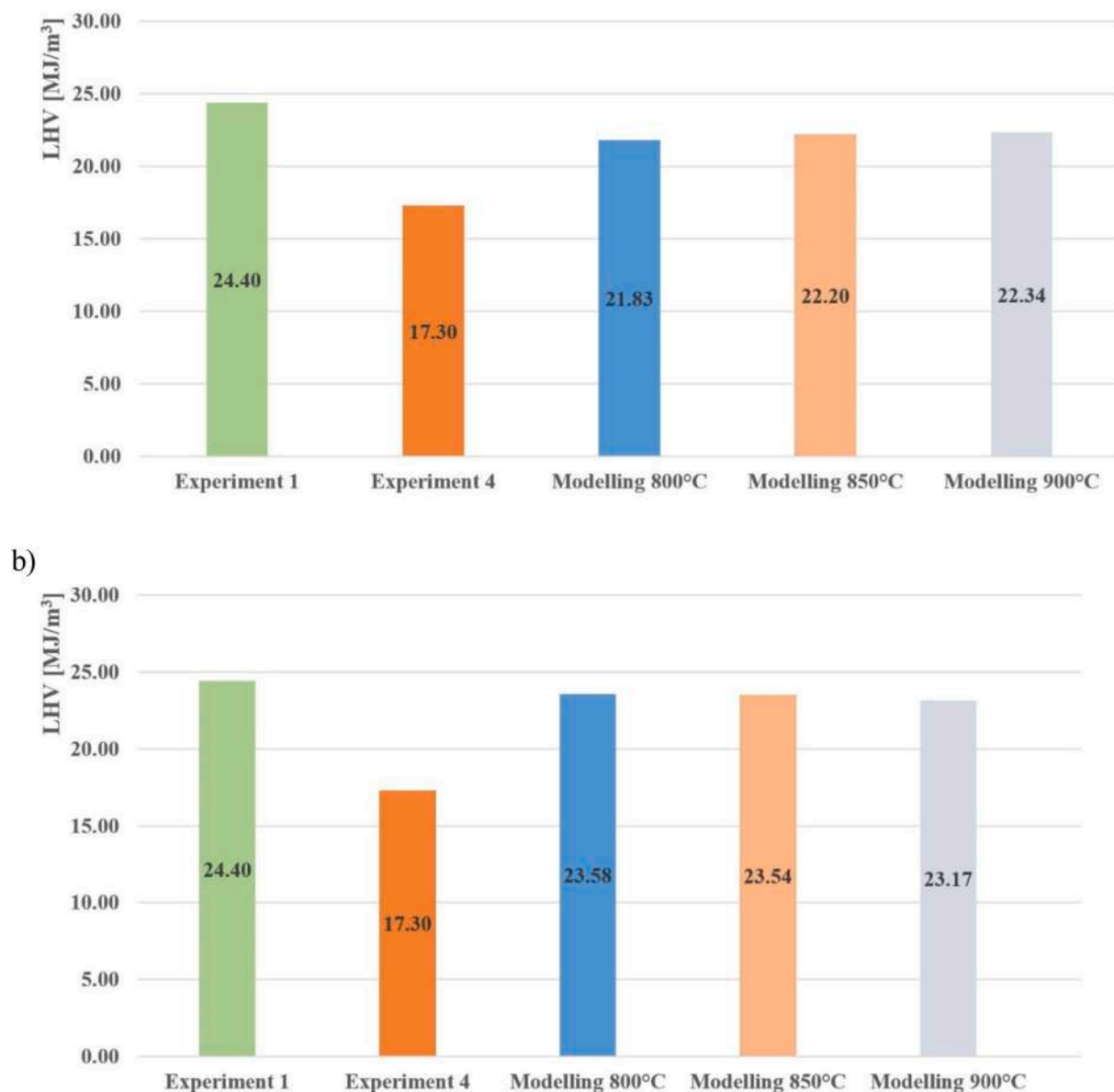


Fig. 11. Comparison of calorific value of pyrolytic gas: a) residence time 2 s; b) residence time 30 s.

compounds with longer carbon chains, i.e. heavy hydrocarbons, as well as their aliphatic and cyclic derivatives which were subject to condensation, were not determined. The concentrations of flammable compounds presented in Fig. 10 translate into a high calorific value of pyrolysis gas, amounting to even 24.4 MJ/m³ for the experiment, while for the modelling it was 23.58% 24.4 MJ/m³ (at the temperature of 800 °C and residence time of 30 s) (Fig. 11). The calorific value was calculated based on the calorific values of the combustible gases and their share in the pyrolysis gas [59]:

$$\begin{aligned}
 LHV = & [H_2] \cdot LHV_{H_2} + [CO] \cdot LHV_{CO} + [CH_4] \cdot LHV_{CH_4} + [C_2H_2] \cdot LHV_{C_2H_2} \\
 & + [C_2H_4] \cdot LHV_{C_2H_4} + [C_2H_6] \cdot LHV_{C_2H_6} + [C_6H_6] \cdot LHV_{C_6H_6} \\
 & + [C_3H_8] \cdot LHV_{C_3H_8}
 \end{aligned}
 \quad (1)$$

It should be noted that the high calorific value is significantly influenced by the presence of heavy organic compounds and their derivatives in the wet pyrolysis gas, even up to 30% of the gas volume. These compounds condense, as a result of which pyrolysis oil is obtained. As the preliminary research carried out by the authors of the article shows, there is a possibility of direct management of wet

pyrolysis gas (i.e. a mixture of pyrolysis gas and gaseous oil) in high-temperature heating chambers, where the temperature reaches 1300 °C. Such a high temperature favors the disposal of the problematic liquid fraction, i.e. pyrolysis oil, leading to measurable economic benefits. The proposed solution is described in detail in the paper [60].

4. Conclusion

Based on the conducted research and the obtained results, the following conclusions and statements were formulated:

1. The implementation of pro-ecological solutions in the field of municipal waste management is currently one of the priorities of waste management strategy. It is also an important marketing asset in the market activity of enterprises dealing with the management and processing of municipal waste.
2. RDF made from personal protective equipment and other wastes using during the pandemic (e.g. plastic packaging) has a great energy potential because it consists of plastic, paper and textiles. RDF

characterises high carbon and hydrogen contents and low moisture content what makes it feedstock suitable for thermal conversion.

3. The results of the research and calculations presented in the article clearly demonstrate that pyrolysis, due to the large yield of high-calorific pyrolysis gas (c.a. 50% of $H_2 + CO$ in pyrolysis gas), is a future direction of waste management, especially plastic waste generated during the pandemic. This gas can be used as a substitute for fossil fuels for energy production. The average HHV of obtained gas was 20 MJ/m^3 .
4. The solid residue obtained from pyrolysis can find application as a solid fuel and as well as can be a good substrate for active carbon production.
5. The microstructure and surface topography of the individual components of the char are highly variable, which can be explained by the heterogeneity of the material subjected to thermal conversion and the diversity of the chemical composition of its individual components.
6. The computer simulations carried out by means of Ansys Chemkin-Pro software show the possibility of predicting the chemical composition of gaseous products of waste pyrolysis.
7. The obtained high calorific value of the pyrolysis gas in the range of $18.4\text{--}24.4 \text{ MJ/m}^3$ encourages wider use of the waste pyrolysis process in order to obtain secondary fuels with promising energy parameters. It will contribute to a further reduction in the amount of landfilled waste, and thus to the creation of environmentally friendly, circular waste management.
8. The over-sieve fraction of municipal waste owing to significant differences in the composition of waste, and thus fluctuations in the composition of the obtained pyrolysis gas should be an addition to the charge of a homogeneous fraction, e.g. uniform plastic waste. It seems that such treatment could achieve satisfactory stability of the pyrolysis gas.
9. Current literature reports indicate that it is possible to combine the pyrolysis process of municipal waste with energy recycling and the use of pyrolysis gas as a renewable energy source employed to produce electricity, which could be the primary source of power for a pyrolysis reactor. The entire recycling process, both in terms of materials and energy, can be carried out in plants handling the collection and sorting of municipal waste and recyclable materials. The obtained gas could be successfully used as an alternative fuel to power a gas turbine or used in cogeneration instead of natural gas. All such activities will contribute to lessening the impact on the natural environment, while effectively reducing the amount of landfilled municipal waste, with the use of alternative energy generated on site.

CRedit authorship contribution statement

Monika Zajemska: Conceptualization, Methodology, Formal analysis, Validation, Writing – original draft, Writing – review & editing. **Aneta Magdziarz:** Conceptualization, Methodology, Supervision, Project administration, Investigation, Writing – review & editing. **Józef Iwaszko:** Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Magdalena Skrzyniarz:** Data curation, Writing – review & editing. **Anna Poskart:** Data curation, Formal analysis, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Perspective

The role of calorific waste in transformation of iron and steel industry towards sustainable production

Monika Zajemska^a, Marcin Sajdak^{b,*}, Józef Iwaszko^a, Magdalena Skrzyniarz^a, Anna Biniek-Poskart^c, Andrzej Skibiński^c, Artur Maroszek^d

^a Czestochowa University of Technology, Faculty of Production Engineering and Materials Technology, 19 Armii Krajowej Ave., 42-200, Czestochowa, Poland

^b Silesian University of Technology, Faculty of Energy and Environmental Engineering, Department of Air Protection, Center of New Technologies, 22 B Konarskiego Ave., 44-100 Gliwice, Poland

^c Czestochowa University of Technology, Faculty of Management, 19 Armii Krajowej Ave., 42-200, Czestochowa, Poland

^d LIBERTY Steel Group, 22 Kucelińska Ave., 42-207 Czestochowa, Poland



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The iron and steel industry, due to its economic potential and importance for the economy, is classified in most countries in the world as an industry of strategic importance. Steel and steel products are the basic material in engineering applications, used by most sectors of the world's economies. The role of this material is therefore of particular importance. On the other hand, the iron and steel industry is one of the most energy-intensive and carbon-intensive industries in the world. It is worth noting, however, that in the face of energy and environmental pressure to reduce carbon dioxide emissions and achieve carbon neutrality, the iron and steel industry has great potential and opportunities to increase its energy efficiency, reduce carbon dioxide emissions and, as a result, promote sustainable development. Nevertheless, numerous scientific works indicate that the transition in the metallurgical industry to sustainable production towards low-emission production processes is unfortunately, costly and difficult as it requires the implementation of new technological procedures as well as adaptation works and extensive tests. Nonetheless, it is necessary to incur these costs in the near future. According to Shukla (2022), there are economic and technological reasons to replace fossil fuels in metallurgical processes with renewable fuels based on biomass. In particular, this applies to biochar, which appears to be a suitable replacement for conventional carbon in aerobic steelmaking (Shukla, 2022). However, it should be emphasized that raw biomass, owing to its high humidity, low carbon content and low calorific value, is not suitable for direct use in

metallurgical processes and requires transformation by means of thermal conversion, e.g. pyrolysis or torrefaction (Iwaszko et al., 2020) into biochar. As indicated in the literature (Mousa et al., 2016), biomass can be used in the iron and steel industry in the following processes: coke-making for the production of bio-coke; the sintering process for the production of bio-sinter, pelletizing/briquetting for the production of bio-composites and/or bio-briquettes, the partial replacement of nut coke, coke or PC in blast furnaces and the bio-re carburization of steel in ladle furnaces (Fig. 1).

In the context of environmental protection and sustainable development, it is therefore important that as much energy as possible is obtained from renewable sources, e.g. bio-coal, to carry out metallurgical processes. Already a 20% share of energy produced from biochar would give measurable effects in the form of a significant reduction in the relationship between the amount of carbon dioxide from non-renewable fossil fuels and the amount of carbon dioxide from renewable sources. Even partial offsetting of carbon dioxide emissions should thus be an obligatory element of the strategy of every enterprise dealing with metallurgical production. Such activities should also be supported by national governments through a system of incentives, soft loans for the implementation and transformation costs, or offering other forms of support, e.g. training, tax exemptions, etc. In this case, activities aimed at achieving sustainable development will not only meet global trends, but also an attestation of environmental awareness. A way to improve

* Corresponding author.

E-mail address: Marcin.Sajdak@polsl.pl (M. Sajdak).

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energy efficiency, expressed in the reduction of fuel consumption, is also to use the potential of post-process gases from the thermal conversion of waste. An example is the application of gas from biomass torrefaction for firing heating furnaces employed to heat the charge before plastic processing (Szwaja et al., 2021). The authors (Szwaja et al., 2021) showed that despite the relatively low calorific value of torgas (approx. 6 MJ/Nm³), it is a profitable undertaking, and an additional benefit of the proposed solution is the possibility of biochar production. The heat from the flue gas with a temperature of about 400 °C would be used to heat the biomass in the torrefaction reactor, which would also increase the efficiency of the feed heating process. The method of utilizing wet torgas in a furnace with an oxygen atmosphere of 1300 °C, proposed by Szwaja et al. (2021), may in the future eliminate the problem of the disposal of the problematic fraction obtained in the torrefaction process and thus increase the attractiveness of biochar production (Yang et al., 2022). The energy use of torgas (or other gases from thermal conversion of waste, e.g. pyrolysis, whose calorific value is much higher) may also

contribute to reducing the consumption of natural gas, which ultimately will allow the diversification of fuel and energy sources, while bringing measurable economic benefits.

As a conclusion, the metallurgical industry is one in which there is undoubtedly the possibility of effective use of fuels from renewable sources. The use of biochar or, for example, gases from the thermal conversion of waste is in this case not only a manifestation of care for the natural environment, but also an action that is fully economically justified. Despite the investment and adaptation costs that the company must incur in the initial phase of technological transformation, in the long run the use of the above-mentioned materials can bring measurable benefits to the steel industry, which will largely compensate for the incurred costs. The immeasurable ecological benefits, i.e. the reduced negative impact on the natural environment, e.g. due to limiting the exploration of natural resources, should also be remembered. Surpluses and unused amounts of char from biomass may also be an effective element of carbon dioxide sequestration in the long term. The prospects

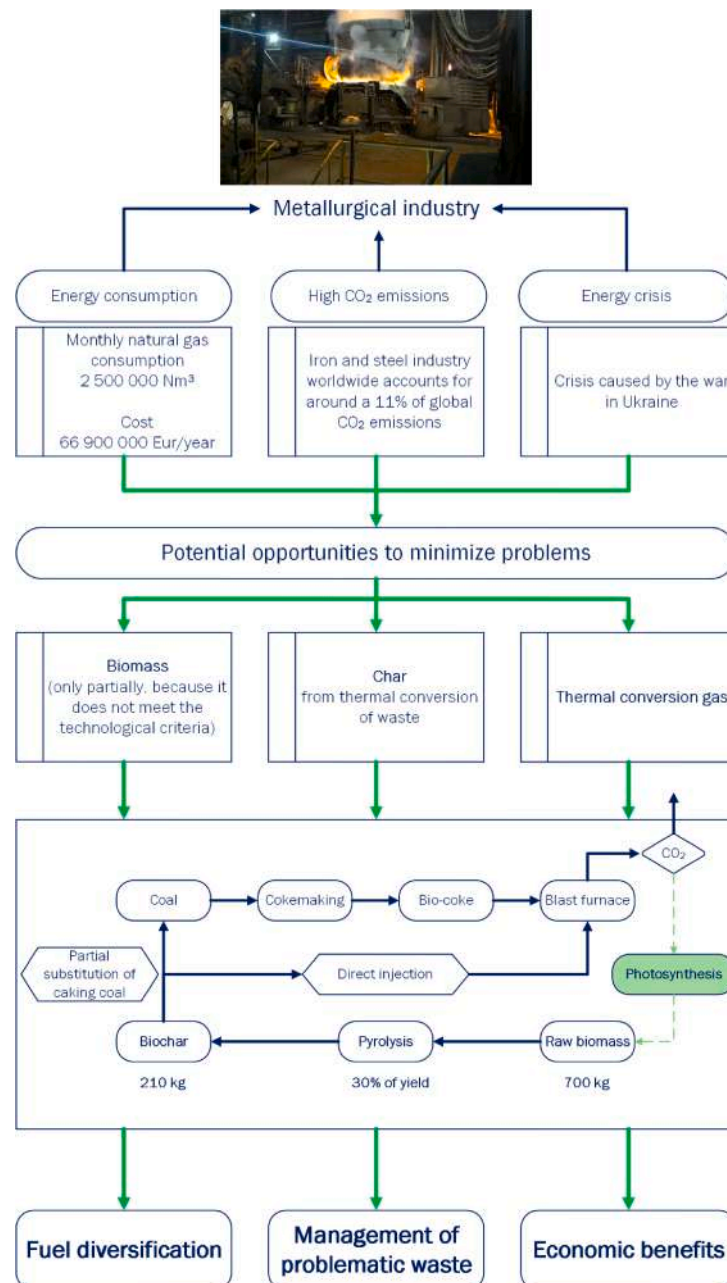


Fig. 1. Directions of calorific waste management in steel industry.

and directions of changes in the steel industry seem to be clearly outlined. Nevertheless, the dynamics of these changes will depend on many factors, including the popularization of solutions promoting ecological behaviour or the equally important substitution of traditional energy resources with materials from renewable sources. The authors were also guided by such premises when preparing this article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Review

The Application of Lignocellulosic Biomass Waste in the Iron and Steel Industry in the Context of Challenges Related to the Energy Crisis

Anna Biniek-Poskart ¹, Marcin Sajdak ² , Magdalena Skrzyniarz ³ , Jakub Rzącki ³, Andrzej Skibiński ¹ 
and Monika Zajemska ^{3,*} 

¹ Faculty of Management, Czestochowa University of Technology, 19 B Armii Krajowej Ave., 42-200 Czestochowa, Poland; a.biniek-poskart@pcz.pl (A.B.-P.); andrzej.skibinski@pcz.pl (A.S.)

² Department of Air Protection, Faculty of Energy and Environmental Engineering, Silesian University of Technology in Gliwice, 44-100 Gliwice, Poland; marcin.sajdak@polsl.pl

³ Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology, 19 Armii Krajowej Ave., 42-200 Czestochowa, Poland; magdalena.kocyba@pcz.pl (M.S.); jakub.rzacki@pcz.pl (J.R.)

* Correspondence: monika.zajemska@pcz.pl

Abstract: This review presented a comprehensive analysis of recent developments in research regarding the use of lignocellulosic biomass products in the iron and steel industry. The role of lignocellulosic biomass used as a source of energy as well as reducing agents in iron and steel sector in the era of energy crisis served as the foundation for this review. Attention has been paid to different biomass characteristics as well as pretreatment methods and conversion products of biomass. The present review also included some issues of energy management system in the steel industry. Furthermore, the possibilities of replacing fossil energy carriers with lignocellulosic biomass in the steel and iron industry was reviewed focusing on advantages, challenges, and future prospects. The present process and product quality criteria, which biomass-derived fuels must also meet, was discussed. This paper compiled the most current developments in biomass metallurgical research to serve as a source for the theoretical foundation as well as for the development of practical applications. The novelty of this study lies in the comprehensive discussion of the lignocellulosic biomass application in the iron and steel industry that are so far unpublished.

Keywords: iron and steel industry; lignocellulosic biomass; biomass waste management; energy management; thermal processing



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1. Introduction

The current state of affairs in the energy sector raises global concerns as well as forces people and nations to diminish the use of fossil fuels and save energy. In the coming years, problems with the availability and high prices of coal, oil, and natural gas for the energy, heating, and steel industry are anticipated. That situation could, of course, be the result of less extraction of this raw material and disconnection of the supply chain from the east. The conflict between Russia and Ukraine has led to various disturbances, and one of the most important areas of its impact is the energy market. The crisis that affected this market is a derivative of the European Union's high dependence on supplies of Russian energy resources, without which no economy is able to function. This situation, caused by unprecedented inflation and skyrocketing fossil fuels prices, has had a serious impact on public infrastructure, as well as industrial and private recipients, prompting decision-makers to discuss changes in the rules of operation of European electricity markets. In addition, coal futures prices are expected to increase due to the anticipated sanctions on coal imports from Russia. The prices of futures contracts, which were record high in 2022,

reflect the price for the next year, due to threats regarding a possible shortage of generation capacity, or owing to future natural gas prices.

The energy crisis has also inevitably left its mark on the metallurgical sector steel producers in Europe have been compelled to a halt or to reduce production due to rising energy prices as reported by the Reuters. The second largest steelmaker in the world, ArcelorMittal, has also shut down a blast furnace in Germany, France, Spain, and Poland. It predicts that its 25% output in Europe would be around 17% lower than a year ago. Even though the eastern Belgian facility of stainless steel manufacturer Aperam boasts four wind turbines and more than 50,000 solar panels, work has been halted due to rising energy costs [1]. Concurring with the most recent press reports, the current circumstances may have a critical effect on the course of the change leading to expediting the resignation from traditional fossil fuels in Europe as well as in the world.

The steel sector is regarded as a high user of carbon and fossil fuels. In general, there are four different routes in steel production: BF-BOF, i.e., blast furnace/basic oxygen furnace; EAF, i.e., melting of scrap in an electric arc furnace; DRI-EAF, i.e., direct reduction/electric arc furnace, as well as SR-BOF, that is smelting reduction/basic oxygen furnace [2], which is shown in Figure 1.

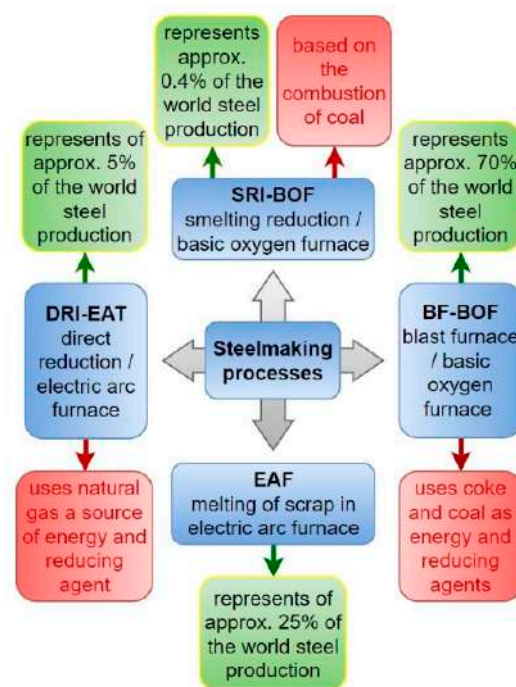


Figure 1. Four main routes of steel production [2].

Metalworking processes require extremely high temperatures, which makes them among the industry's most energy-intensive processes. One steelworks needs more energy than an agglomeration of one million people [3]. Only in production facilities for the preparation of raw materials, about 80 kg of fossil coal are used for every ton of utilized output. Per ton of sinter output, the sintering machine uses around 50 kg of fossil fuel [4]. Electric or oxygen processes are used to make steel, whereas the oxygen route consumes a huge amount of fossil fuels and, hence, generates significant emissions of CO₂. According to the data that are currently available, it is estimated that global steel manufacturing accounts for 5–6% of all greenhouse gas emissions [5]. According to Shukla [6], typically, 0.8 tons of coal are needed to produce 1 ton of crude steel, while 1 ton of hot metal produced in a coke blast furnace leads to 1.9 tons of CO₂ emissions. The metallurgical industry is inclined to search for new solutions in the field of energy production based on energy carriers other than fossil fuels for yet another reason, which is ecology and the pursuit of sustainable development. Iron and steel production are crucial to economic growth,

but they are also the leading industrial source of CO₂ emissions. As the World Steel Association claimed in 2022, 1878.5 Mt of crude steel were produced globally. According to the same group, the demand for steel would increase by 2.2% to 1881.4 Mt in 2023 [7]. The International Energy Agency (IEA) [8] reports that steel has a carbon footprint of 1.4 tons per ton produced, whereas McKinsey and the World Steel Association place that number at 1.85. This is a weighted average of the two primary global steel manufacturing processes. The “primary” and “secondary” methods are generally referred to as the route of BF-BOF, i.e., blast furnace-basic oxygen furnace as well as EAF, i.e., the electric arc furnace. These two technologies have respective CO₂ footprints of 1.987 and 0.357 tons per ton of steel produced. However, in rare instances, the amount of CO₂ produced per metric ton of steel might reach 3. The variations amongst steel producers can be substantial. It all depends on how the steel is made, and it appears that the figures given above are an average of two separate production processes [9].

According to the report elaborated in cooperation with World Bank [10], the European Green Deal, i.e., Europe’s new growth strategy, intends to reduce pollution, make industry and transportation sustainable, achieve climate neutrality in Europe by 2050, and grow the economy through green technologies, which may become a development impulse for the industry, including the steel industry. A promising and viable alternative approach to implement European Green Deal is to employ biomass products in the iron and steel industry as a source of energy as well as reducing agents. Recently, new and improved existing solutions for the use of biomass in the iron and steel industry have been sought. Lignocellulosic biomass is regarded by Yadav et al. [11] as an abundantly accessible renewable feedstock for the generation of biofuels that has the potential to minimize reliance on petrochemical refineries. In contrast to other bioresources, lignocellulosic waste is unique due to its quantity, renewable status, biodegradability, and biocompatibility. However, the limited solubility and processability of natural lignocellulosic materials reduce their use. Thus, pretreatment is necessary to utilize it later as an energy source or renewable resource. Physical or mechanical pretreatment, such as milling, grinding, or chipping, is the first step in processing lignocellulosic biomass. It aims to break the complex structure of lignocellulosic biomass. Chemical pretreatment, on the other hand, entails the pretreatment of various lignocellulosic feedstock types employing a range of chemical agents, including acids, ammonia, alkalis, ozone, peroxide, deep eutectic solvents, and ionic liquids [12,13].

A great deal of work has been carried out over the years to investigate the use of biomass-based materials as a fuel and reductant in primary metal production in the place of fossil fuel carbon sources. In addition to being CO₂ neutral, biomass material is also probably lower in S, Cl, N, as well as other heavy metals, which are detrimental to the environment, human health, and metal quality [5]. One way to achieve a green low-carbon iron and steel industry is to replace conventional fossil fuels with biomass energy. In addition, it is also important to accelerate the adaptation of the industry’s energy structure to modern, future-oriented technologies [14]. Thus, the demand for investments that boost energy efficiency will rise in the nearest future. The study presented in this paper was focused on biomass applications as a fuel source replacing coal during metallurgical processes.

The novelty of this study lies in the comprehensive discussion of the lignocellulosic biomass application in the iron and steel industry that are so far unpublished. The previous, scarce research and the literature gap on the use of lignocellulosic biomass in the iron and steel industry and the current world energy crisis prompted the authors of the article to conduct a literature review in this topic. When we reviewed the literature, we found that there are not many papers that describe in detail replacing coke with charcoal from lignocellulosic biomass, and there are not much data on the specifics of the charcoal that is utilized.

2. The Role of Lignocellulosic Biomass in the Era of Energy Crisis and Decarbonization

The increasing need for energy is accompanied by the depletion of its conventional supplies, namely fossil fuels (coal, oil, and natural gas), and the consequent rise in environmental degradation. The usage of energy from renewable sources has grown in popularity as a result of these causes. Biomass is thought to be a promising renewable energy source. The use of substitute fuels from conventional fossil fuels is highly important, in view of the fact that iron and steel are among the world's largest energy-consuming and greenhouse-gas-emitting industries. The application of lignocellulosic biomass in the steel and iron industry has the potential to accelerate the transition of this sector to a low-carbon and environmentally friendly future by lowering the emissions of CO₂ and the consumption of fossil fuels. Biomass metallurgy is the name given to metallurgical processes that employ carbon and hydrogen-rich renewable biomass as the primary energy source and reducing agent to recover metals [14].

The possibilities of using alternative renewable sources as fuels in the various processes of the iron and steel industries have been examined in a number of studies [6,15–17]. Biomass can be used in such steelmaking processes, e.g., in the blast furnace, coke-making, and sintering. Various steelmaking techniques were addressed together with current advancements toward partial or complete replacement of fossil fuels by renewable energy based on biomass. Kieush et al. [4] showed the potential of employing secondary carbon bio-carriers, i.e., biomass, biochar, torrefied biomass, biocoke, or charcoal for iron and steel production. The four main routes of steel production, namely the melting of scrap in an electric arc furnace (scrap/EAF), blast furnace/basic oxygen furnace (BF/BOF), smelting reduction/basic oxygen furnace (SR/BOF), and direct reduced iron/electric arc furnace (DRI/EAF) were described in their work.

To achieve a reduction in the demand for fossil fuels and low CO₂ emission targets, a change in the ways that energy is produced and consumed is necessary. Biomass metallurgy has the advantage of being carbon neutral and reducing CO₂ emissions significantly when compared to traditional coal metallurgy [14]. Biomass can, under the correct circumstances, be viewed as a carbon-free resource, making it a desirable choice for lowering emissions from the manufacture of iron and steel. According to the IEA's bioenergy program, if produced sustainably, bioenergy can be carbon neutral within the biospheric carbon cycle due to the fact that the carbon being released during combustion has already been removed from the atmosphere and will be removed once more as the plants regrow. Furthermore, after transformation, the physicochemical properties of biomass can be comparable to those of coal. Because of its high carbon content, which ranges from 39 to 57%, lignocellulose biomasses in particular seem to be a promising, sustainable, and cost-effective solution. A remarkable opportunity exists to develop alternative fuels as a replacement for fossil fuels thanks to readily available, affordable, and renewable lignocellulosic biomass, especially when talking about a significant part of agricultural waste, which is underutilized and inadequately handled. For instance, in Nigeria, approx. 30% of agri-food wastes produced per year are left after harvest without any further application.

2.1. Biomass Characteristics

Growing interest has been shown in recent years in creating pyrolysis routes from lignocellulosic biomass to produce biofuels. Plant material known as lignocellulosic biomass is not employed in food or animal feed [18]. Lignocellulosic biomass is the most energy-efficient type of biomass because lignin and cellulose are characterized by a large share of "waste" mass, which is suitable for use as a source of thermal energy. It mostly comprises yard trimmings, energy crops, forestry waste, and agricultural waste. After coal and petroleum products, lignocellulosic biomass is considered as one of the largest source of energy. It is one of the best possibilities for the manufacturing of chemicals and fuel intermediates because of its widespread availability around the globe, low cost, and minimal greenhouse gas emissions [19,20]. More than 200 billion tons of lignocellulosic biomass

is thought to be produced annually on Earth. Lignocellulosic biomass mostly comprises lignin (15–25 wt%), hemicellulose (20–40 wt%), and cellulose (30–50 wt%) [21]. Ash, lipids, and proteins make up the remainder of lignocellulosic biomass. Depending on the species, lignocellulosic biomass can have different chemical and elemental compositions. The primary factor in determining the overall calorific value of a substance is its carbon content, which accounts for 34.1 to 53.5 weight percent of the biomass. In comparison to fossil fuels, the nitrogen (1.8 wt%) and sulfur (0.1–0.6 wt%) concentrations of biomass are often rather low [22]. Given that each fraction travels through a separate set of decomposition routes under a different set of reaction circumstances, the relative quantity of the biomass component has a considerable impact on both the output of biomass products and their chemical composition [23].

Raw biomass has a number of drawbacks, including a low calorific value, high moisture content, high oxygenated volatile materials (VM) content, hygroscopic character, and low energy density, varying composition and properties or contamination when low quality sources are used. While VM can range from 63 to 88 weight percent, the fixed carbon (FC) content of raw biomass typically ranges from 9 to 25 weight percent [4,24,24]. A higher volatile matter concentration causes ignition to be quicker and easier with a lower ignition temperature than coal. It offers improved combustion, but because it burns quickly, some unburned carbon ends up as ash. Additionally, a higher VM produces flammable vapors that are difficult to manage and useless for sintering operations until additional preparations are made [25]. Biomass has an energy density that is between 10 and 40% lower than that of coal, and its heating value is around half that of coal [26]. On the other hand, as reported by Jha et al. [26], in comparison to coal, biomass has less sulfur, which lowers SO_x emissions. Morón et al. [27] studied the impact of fuel sulphur content in blends of coal with biomass on the conversion into SO₂. They noticed that the emissions of SO₂ were drastically decreased by mixing biomass with coal. Furthermore, a higher content of volatile matter in biomass ensures easier, more rapid ignition, as well as lower ignition temperature. An interesting result of studies was presented by Mahanta et al. [28] that concern blending high sulfur low-rank North East Indian coal with biomass of Acacia as an additive in order to reduce the amount of sulfur and the ash content as well as to enhance the combustion performance. The addition of biomass appears to improve coal's ignition and burnout characteristics because to its improved reactivity and greater volatile release at lower temperatures. However, the moisture content, which lowers the heat value, is the main flaw of biomass. The moisture content of biomass typically ranges from 3% to 63%, although it can reach 91%. Because biomass mostly consists of organic materials generated from plants and crops, it has a greater moisture content. Since biomass has lower levels of nitrogen and sulfur, it produces fewer emissions of NO_x and SO_x. According to Dubinin et al. [29], biomass generally has 10 times less sulfur than coal and coke. The properties of different types of biomass are described in Table 1.

Table 1. Comparison of physicochemical properties of biomass.

Biomass	Ultimate Analysis (%)					Proximate Analysis (%)				Source
	C	H	N	S	O	M ¹	VM ²	FC ³	A ⁴	
Rice straw	36.2–47.46	5.2–6.44	0.7–0.83	-	40.3–45.15	4.98	81.54	16.46	10.82–17.6	[30]
Wheat straw	41.8–45.5	5.5–5.7	0.7–1.0	-	35.5–47.9	7.1	76.7	9.2	7.0	[30]
Barley straw	45.41	6.1	1.18	-	46.21	4.90	78.8	11.83	6.43	[30]
Corn straw	45.75	5.93	0.94	0.11	43.69	4.21	-	-	5.91	[30]
Sugarcane straw	41.88	5.87	0.47	-	41.72	3.12	87.61	3.22	9.17	[30]

Table 1. Cont.

Biomass	Ultimate Analysis (%)					Proximate Analysis (%)				Source
	C	H	N	S	O	M ¹	VM ²	FC ³	A ⁴	
Rape straw	42.21	5.54	0.42	0.07	51.76	-	-	-	3.69	[30]
Mustard straw	54.46	6.29	0.5	-	38.75	3.99	75.55	15.44	5.02	[30]
Moringa husk	48.84	6.53	-	-	-	1.47	76.6	-	2.36	[31]
Eucalyptus husk	50.1	5.42				5.77	68.73		2.43	[31]
Sugarcane bagasse	46.4	4.68	-	-	-	7.03	75.03	-	4.33	[31]
Elephant grass	40.0	5.36	-	-	-	0.1	69.95	-	13.5	[31]
Rice husk	43.4	4.33	-	-	-	0.1	73.18	-	9.55	[31]
Corn cob	45.5	6.7	-	-	-	0.79	81.31	-	1.16	[31]
Corn straw	44.8	6.8	-	-	-	0.31	81.68	-	1.58	[31]
Oil palm tree trunk	40.75	6.47	0.51	-	-	-	-	-	-	[32]
Mesocarp fibers	45.2	9.04	3.12	0.1	42.53	-	75.23	18.42	5.35	[33]
Palm kernel shells	46.3	5.72	0.7	0.64	47.6	9.4	69.8	16.8	4.0	[34]
Hazelnut shells	50.3	6.3	0.7	-	43.2	9.0	76.7	22.5	0.8	[35]
Switch grass	43.2	5.89	0.52	0.16	50.23	6.25	71.21	19.14	3.4	[36]
Rice straw	37.18	5.81	0.62	-	56.39	9.8	76.32	9.08	13.91	[37]
Coconut shell	48.6	5.97	0.62	1.09	43.8	10.5	71.1	17.6	0.8	[34]
Pine Sawdust	49.5	7.1	0.5	-	42.8	5.0	84.5	15.4	0.1	[35]

“-” denotes not detected/not reported; ¹ moisture; ² volatile matter; ³ fixed carbon; ⁴ ash.

Due to the raw biomass’s low calorific value, high moisture and oxygen content, and extremely changeable composition and characteristics, the direct conversion of biomass into energy is not very profitable [38,39]. Therefore, techniques for increasing the energy characteristics of biomass are actively being investigated.

2.2. Methods of Biomass Conversion

It would be ideal to create items that either outperform current fuels and/or reductant technologies or reduce any physical flaws. Thus, effective methods of biomass conversion are required to create chars that are chemically equivalent to coal or coke. In order to obtain bio-substitutes with qualities permitting a complete or at least partial substitution of fossil fuels in metallurgical processes, pre-treatment is, therefore, necessary. To improve the fuel characteristics, increase the heating value, and to apply to various plants in the iron and steel sectors, agricultural waste can be thermochemically converted into biochar, bio-oil, and syngas [6]. Thus, thermal processing such as torrefaction [40,41], pyrolysis [42,43], gasification [44], liquefaction [45,46], or hydrothermal carbonization [47–49] can be applied. Promising results of lignocellulosic biomass thermochemical processes [50] were achieved by the authors, especially in the case of torrefaction [51,52], pyrolysis [20,53,54], and gasification and co-gasification [55–57].

Figure 2 shows methods of conversion of biomass through modern and traditional way as well as products generated during these processes. Furthermore, typical applications

of biochar were also presented. In turn, Table 2 constitutes a compilation of individual processes and their main characteristics.

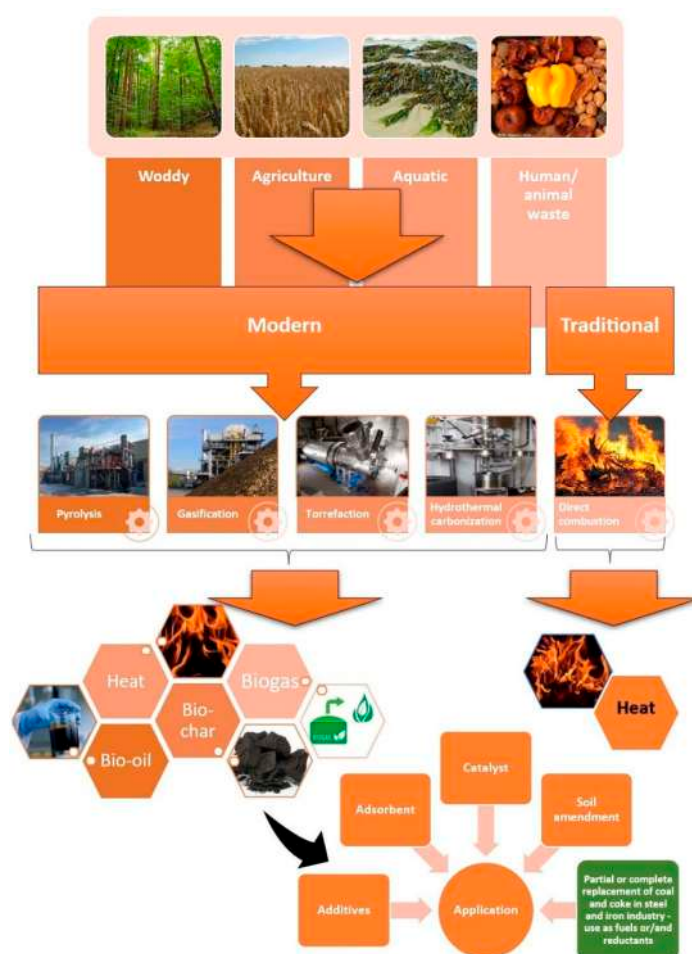


Figure 2. Methods of conversion and use of biomass and its products [58–63].

Table 2. Compilation of characteristics of individual processes.

Process	Reaction Temperature °C	Conditions	Product	Composition of Product (m-%)			Source
				Solid	Liquid	Gas	
Pyrolysis, slow	180–480	Residence time: 15 min to even several hours; absence of air (oxygen)	Biochar	>60	25–30	10–15	[64–67]
Pyrolysis, fast	Above 500	High heating rate [68]; for a few seconds; absence of air	Bio oil	20–30	30–70	20–30	[68–71]
Gasification	600–1400	With the use of oxidizing agent; under higher pressure (1–5 MPa)	Synthesis gas	10	5	85	[66,72,73]
Torrefaction	200–350	For 15–30 min without presence of air	Biochar	80	15	5	[52,74,75]

Table 2. Cont.

Process	Reaction Temperature °C	Conditions	Product	Composition of Product (m-%)			Source
				Solid	Liquid	Gas	
Hydrothermal Carbonization	160–250	Mixed with saturated water-steam; from a few minutes to even few hours	HTC Carbon	50–80	5–20	2–5	[66,72,76]
Combustion	Wide range depending on the fuel type	With air excess	Heat	-	-	-	[72]

The thermochemical process of pyrolysis, which can result in the production of pyrolytic gas, biochar, and bio-oil, typically occurs at temperatures within the range between 400 and 1000 °C and without access to air [77]. Slow pyrolysis produces charcoal primarily, and calls for a slower heating rate, lower temperature, and a longer residence period. In contrast, bio-oil is the primary end product of fast pyrolysis, which is carried out at a rapid heating rate and for a brief period of time [78]. Fast pyrolysis is the process of rapidly heating biomass to high temperatures without the presence of air, more precisely without oxygen. It takes place at high temperatures between 300 and 700 °C, with a quicker heating rate of 10 to 200 °C/s, a brief solid residence duration of 0.5 to 10 s, and feedstock with a tiny particle size (1 mm) [79]. Pyrolysis and gasification are both thermochemical processes, although gasification takes place at much higher temperatures of around 1000–1400 °C and in the presence of less oxygen [77].

To enhance the qualities of raw biomass, light, medium, or severe torrefaction can be used depending on the intended final attributes of the solid product. Torrefaction is one of the most promising methods of biomass valorization. It typically takes place at temperatures between 200 and 350 °C, under atmospheric pressure, with inert gases present, and with residence times between 15 min and 3 h (depending on the kind of reactor and the parameters of the raw material) [41,80,81]. Torrefaction produces solid (biochar), liquid, and gaseous byproducts. The solid material (the so-called torrefied/carbonate) constituting approx. 80% has a hydrophobic character and a uniform structure, with a low moisture content, increased regrindability, low bulk density, and high calorific value. Thanks to the torrefaction process, biomass gains new properties that are particularly beneficial when used for energy purposes. By altering the shape, eliminating water and oxygen through carboxylation and dehydration processes, as well as damaging the fibrous structure of biomass, the primary goal of this process is to enhance the qualities of the biomass. Torrefaction eliminates most of the disadvantages of biomass. Torrefied biomass acquires unique physical–chemical characteristics that are particularly advantageous when utilized as a fuel for energy production, such as during combustion. The biomass is heated and partially devolatilized during torrefaction. It loses bulk while maintaining its energy level. The majority of the unfavorable characteristics of biomass are eliminated during the torrefaction process, resulting in the production of fuel with a greater carbon content, a higher calorific value, a higher energy density, improved grindability, hydrophobicity, and resistance to biodegradation. As a result, it may be possible to lower the cost of managing, storing, and transporting biomass [52]. Torrefaction is a less aggressive heat-treatment method than pyrolysis, which enhances the characteristics of biomass without harming the high molecular components. Torrefied biomass also contains less ash than biochar produced during the pyrolysis process. Torrefaction can also contribute to the minimization of carbon dioxide emissions, which is less by approx. 50 kg/t of steel. Furthermore, the distribution of biomass constituents is altered by the torrefaction process. At temperatures between 200 and 900 °C, lignin slowly breaks down. In turn, cellulose and hemicelluloses begin to break down at temperatures between 200 and 400 °C. Torrefaction lowers the amount of

hemicellulose from 22% to 4.6% at 300 °C while progressively destroying the cellulose and increasing the amount of lignin. As a result of torrefaction, biomass slowly decomposes, dries up, and simultaneously releases a small amount of volatile organic chemicals. This leads to changes in the torrefied biomass composition. The hydrogen and oxygen contents of torrefied biomass are lower, while the carbon content is higher [4]. Furthermore, because raw biomass has such a high percentage of active ingredients (hemicellulose and cellulose), it often exhibits characteristics of high reactivity and low thermal stability, which indicate a significant danger of unprompted combustion and deterioration during storage and transit. It has been demonstrated that biomass hydrophobicity and fuel quality may be improved with torrefaction pretreatment, which also lowers the likelihood for spontaneous combustion [82]. The torrefied biomass can either be pumped into the BF or utilized directly in the synthesis of carbon composite agglomerates (CCAs), coke, and sinter. Secondary carbon bio-carriers might be used to produce biocoke when the characteristics are altered. Based on the requirements for the carbon-containing material in a specific process, the torrefied biomass can make up anywhere from 3 to 50 weight percent of the feed mixture during the coke-making process. The biocoke that is produced can be used for: sintering iron ores to serve as fuel; BF to perform duties as a fuel and reducing agent; EAF for slag foaming and carburizing; a melter gasifier to produce heat; and serve as a reducing agent [4].

2.3. Biomass Conversion Products

Combustion, torrefaction, slow pyrolysis, quick pyrolysis, and gasification are the primary thermochemical biomass conversion processes. Torrefied biomass, biochar, non-condensable gases (NCG), condensable gases (bio-oil; recovered from pyrolysis gas by cooling), and syngas are the many byproducts. The amount of each conversion product and the percentage of each fraction vary depending on both the procedure in issue and the process parameters [67].

As presented in the report developed by the Technical Research Centre of Finland (VTT) [67], depending on the conversion rate under consideration, there are several potential end applications for the conversion products:

- Torrefaction reduces the surplus oxygen content of the biomass and increases the energy density. Torrefied biomass might be utilized in place of fossil fuels in many combustion applications, such as the production of electricity [75,83,84].
- For wet biomass (or sludge), hydrothermal carbonization is normally carried out in pressured autoclaves at temperatures within the range of 200 and 300 °C. The process purges the solid mass of inorganic chemicals that are water soluble. The product possesses heating properties that are comparable to those of torrefied biomass and a relatively low carbon-to-oxygen ratio [48,66,85,86].
- Slow pyrolysis optimizes the yield of biochar, which may be utilized either directly or after additional processing in a variety of applications, such as replacing coal in combustion, acting as a bio-reducer in the production of metals, enhancing soil, treating water, etc. Condensable and non-condensable hot pyrolysis gases are also produced, and these gases may be used as fuel to substitute fossil-based combustibles in a variety of applications. Bio-oil may be made by collecting the condensable portion [87–90].
- Fast pyrolysis enhances the output of condensable gas-derived bio-oil. Additionally, a small quantity of biochar as well as some NCG are produced. When compared to those produced by slow pyrolysis, the characteristics of biochar are somewhat different, which might limit its potential applications, such as a bio-reducer [91–93].
- In the process of gasification, biomass hydrocarbons completely devolatilize into syngas when enough oxygen is present. CO, CH₄, H₂, CO₂, and smaller quantities of other gases are the main constituents. Syngas can be utilized in combustion to produce hydrogen, Fischer–Tropsch gasoline, Fischer–Tropsch diesel, alcohols, olefins,

oxo compounds, synthetic natural gas (SNG), and ammonia, or as an intermediate product for those processes [44,94,95].

The origin of the biomass on which biochar is based determines its features, and even different tree species will create biochar with variable qualities. The density, strength, and porosity of the biochar, for instance, will be influenced by the density of the tree species. As a result, in order to attain superior qualities, the biochar that is now utilized in the metallurgical sector (in the manufacture of silicon and ferrosilicon) is based on hardwoods. The solid carbon is crucial for metallurgical operations since the carbon that is gassed off throughout the process will not function as a reducing agent. The process parameters that are employed to produce biochar have a significant impact on the yield of solid carbon. A relatively low yield of fixed carbon is normally obtained from traditional charcoal manufacture. When the gaseous tar components spend a longer time in and around the charcoal, the yield can be greatly improved. Compression and densification can boost the tensile strength of biochar. Fuel sources such as coal and biomass come in a wide variety. Energy levels, organic and inorganic contents, and physical qualities are where these variances are most noticeable [96–98]. Nonetheless, the properties of biochar obtained during torrefaction or pyrolysis are more comparable to coal. However, contrary to biochar, which normally has a highly porous structure due to volatiles releasing during the charring process, coals typically have a densely packed structure [99]. The characteristics of different types of torrefied biomass and coal are presented in Table 3.

The results of the computer simulations performed within work [20] allowed the estimated calorific value of the pyrolysis gas to be calculated, which ranged from 20.61 to 25.19 MJ/m³. The high calorific value of gas promotes its further usage in the steel and heating sectors. It is possible to co-combust natural gas with the gas produced by the pyrolysis of lignocellulosic waste, which will result in a reduction in natural gas consumption. The aforementioned information demonstrates that pyrolysis gas may be a great substitute for traditional fuels, while also advancing environmental protection efforts and playing a significant part in the circular economy for biomass. The reduced moisture and oxygen content, as well as an increase in the calorific value and carbon fraction of the solid product, are benefits of thermal biomass treatment that make it more suited to be utilized in several metallurgical processes. However, after being heated, the ash content of biochar increases and its mechanical strength decreases. Numerous studies have concentrated on the use of biochar for metallurgical processes after pyrolysis at temperatures ranging from 350 to 1100 °C. The solid product reduction, which is the most useful for application in subsequent metallurgical operations, is a drawback of high-temperature pyrolysis.

Table 3. Physicochemical properties of coal and biochar from biomass.

Component		Proximate Analysis, wt. %					Ultimate Analysis, wt. %					Source
		M ¹	A ²	VM ³	FC ⁴	S	C	H	N	O	P	
Coal A		1.5	11.0	30.3	58.7	0.68	75.38	4.77	1.54	6.63	-	[100]
Coal B	Subbituminous	16	6.5	29.5	-	0.65	-	-	-	-	0.06	[101]
Coal C	High-VM	2.5	9.0	34.5	-	0.40	-	-	-	-	0.01	[101]
Coal D	Semianthracite	1.5	7.5	12.5	-	0.60	-	-	-	-	0.07	[101]
Coal E	Anthracite	2.0	9.0	6.5	-	0.50	-		-	-	0.01	[101]
Coal F		1.4	11.0	33.6	55.4	0.82	74.49	5.09	1.61	6.99	-	[100]
Coal G		3.8	8.4	23.2	68.4	0.32	82.61	4.78	1.43	2.46	-	[100]
Biochar A	Torrefied softwood	2.0	0.5	69.1	-	0.02	-	-	-	-	0.01	[101]
Biochar B	Semicharcoal (hardwood)	0.7	2.3	33.1	-	0.05	-	-	-	-	0.07	[101]
Biochar C	Charcoal (softwood)	1.0	0.9	6.2	-	0.05	-	-	-	-	0.02	[101]
Biochar D	Charcoal (hardwood)	1.8	3.4	7.6	-	0.09	-	-	-	-	0.10	[101]
Biochar E	Charcoal (mallee)	1.6	3.4	0.3	-	0.04	-	-	-	-	0.0	[101]
Biochar F	Biocoke	0.65–1.35	5.8–10.8	1.4–2.7	87.8–92.4	0.22–0.2	86.38–91.65	-	-	-	-	[4]
Biochar G	Charcoal	0.63	7.73	25.8	-	-	69.7	3.2	-	-	-	[31]
Biochar H	Torrefied sugarcane bagasse	1.41	2.52	78.74	17.33	-	40.0	6.74	0.72	52.54	-	[102]
Biochar I	Torrefied eucalyptus	-	-	-	-	-	56.01	5.99	0.05	36.18	-	[103]
Biochar J	Chlorella sp.	2	12.8	32.4	-	2	35	9.2	3	2.5	-	[104]
Biochar K	Sargassum sp.	2.5	14.2	35	-	2.6	61.5	4.2	2	28	-	[104]
Biochar L		2.30	0.57	19.10	91.6	0.02		2.27	0.38	1.95	-	[105]

Table 3. Cont.

Component		Proximate Analysis, wt. %					Ultimate Analysis, wt. %					Source
		M ¹	A ²	VM ³	FC ⁴	S	C	H	N	O	P	
Biochar M	Safflower seed cake	-	8.20	20.00	7180	-	70.43	3.43	3.36	22.39	-	[106]
Biochar N	Concarpus waste	-	5.27	-	-	-	76.83	2.83	0.87	14.16	-	[106]
Biochar O	Rice straw	7.20	15.40	62.40	14.90	-	44.80	5.10	0.90	49.20	-	[106]
Biochar P	Pitch pine	-	7.90	-	-	-	70.70	3.40	0.60	25.50	-	[106]
Biochar R	Pine sawdust	5.00	0.30	77.70	16.90	-	50.30	6.70	0.20	42.70	-	[106]
Biochar S	Spruce woodchips	-	31.00	-	-	-	74.80	0.14	0.15	4.20	-	[106]
Biochar T	Corn stovers	2.3	58.00	12.70	28.70	-	33.20	1.40	0.81	8.60	-	[106]
Biochar U	Coconut shell	4.4	0.70	80.20	22.00	-	50.20	5.70	0.00	43.40	-	[106]
Biochar W	Peanut shell	1.90	7.80	8.10	82.20	-	93.61	1.99	1.05	3.35	-	[106]
Biochar X	Pine cone	1.20	4.70	6.70	87.40	-	95.16	2.63	1.61	0.60	-	[106]
Biochar Y	Peanut hull	-	9.30	18.10	-	-	81.80	2.90	2.70	3.30	-	[106]
Biochar Z	Switch grass	-	7.80	13.40	-	-	84.40	2.40	1.07	4.30	-	[106]
Biochar AA	Pongamia glabra deoiled cake	4.30	11.60	14.60	69.50	-	75.00	3.26	5.00	12.58	-	[106]
Biochar AB	Jute dust	9.44	10.78	15.07	64.71	-	70.25	2.78	4.04	22.93	-	[106]
Biochar AC	Sugarcane bagasse	1.30	8.57	9.17	80.97	-	85.59	2.82	1.11	10.48	-	[106]
Biochar AD	Coco peat	2.55	15.90	14.30	67.25	-	84.44	2.88	1.02	11.67	-	[106]
Biochar AE	Palm kernel shell	0.00	6.86	12.29	80.85	-	87.85	2.91	1.11	8.14	-	[106]
Biochar AF	Cotton seed hull	6.53	7.90	18.60	67.00	-	87.50	2.85	1.50	7.60	-	[106]
Biochar AG	Soybean cake	1.50	16.80	10.10	71.60	-	83.95	1.48	8.32	6.25	-	[106]
Biochar AH	Sesame	3.40	36.80	22.00	37.80	-	86.64	3.10	6.93	3.09	-	[106]

“-” denotes not detected/not reported; ¹ Moisture; ² Ash; ³ Volatile matter; ⁴ Fixed carbon.

3. Lignocellulosic Waste and Energy Management in the Steel Industry

As reported by the Organisation for Economic Co-operation and Development in their report [107], typically, the iron and steel sector is the second-biggest user of energy among all industrial sectors. Approximately 20% to 25% of the steel plant's total input expenses are made up of energy expenditures. According to the technical report elaborated by the European Commission's science and knowledge service, the Joint Research Centre (JRC) [108], the energy expenses for EU27 plants are the third highest in the world (on average 17% of total production costs). Utilizing less energy while producing the same or even more is known as energy efficiency. It is becoming more widely acknowledged as one of the most significant and economical methods for lowering greenhouse gas (GHG) emissions produced during industrial operations, particularly those in the iron and steel industry. In reality, technological advancements in energy efficiency have the potential to cut industrial energy usage by around 20% [107]. It is significant to note that energy efficiency may raise a company's competitiveness and production in addition to saving energy and lowering GHG emissions. Along with enhanced internal efficiencies that boost the company's value, successful energy efficiency projects frequently have this effect. Identifying and prioritizing the complete spectrum of energy savings potential before making any other significant investment decisions requires the implementation of an energy management system, which is a crucial first step. As reported by McKinsey & Company experts and consultants [109] as well as Danish Energy Agency [110], better energy management, which often involves just operational improvements, has been demonstrated to enable businesses to save up to 10–30% of their yearly energy usage. As a result, operating expenses may be reduced in a manner comparable to that. Companies optimize their industrial systems and increase overall system efficiency monitoring by implementing an Energy Management System (EnMS) in order to improve energy performance. EnMS is known as a systematic method for continuously enhancing energy performance and maximizing energy savings. An EnMS's main goal is to motivate employees at all organizational levels to continuously regulate their consumption of energy. By creating a framework for industrial facilities to monitor their continuing energy usage and find possibilities to deploy energy-saving technology, an EnMS helps enterprises in the iron and steel sector achieve this. Enhanced production and capacity utilization, decreased resource consumption and pollution, and cheaper operation and maintenance expenses are some additional productivity advantages for businesses employing an EnMS. These advantages all promote value creation and, consequently, a company's competitiveness [107].

Energy consumption is a significant contributor to emissions in the iron and steel sector, making energy efficiency improvements a desirable way to cut both pollution and greenhouse gas emissions. A major potential to lower costs and hazards connected with measures linked to reducing the emissions of greenhouse gases and pollutants is to increase energy efficiency. In order to achieve the so-called “triple bottom line”, which focuses on the social, economic, and environmental elements, energy efficiency might, thus, be a useful and productive technique. In the current context, investing in energy-efficient devices is a wise approach for managing steel and iron plants [111].

Different cycles, including heating, cooling, melting, solidification, and processing, are used in iron and steel factory operations. It is an industry that uses large amounts of energy. The decreased energy use of iron and steel plants is of particular importance. For the iron and steel sector to remain competitive, sustainable, able to reduce its environmental effect, particularly greenhouse gas emissions, and improve resource management, energy conservation is essential [111,112]. The worldwide steel sector has a strong interest in energy saving. Energy efficiency strategies and technology address this difficulty and have improved in cost-effectiveness over the past several years, which has been beneficial during periods of high and unpredictable energy costs and intense concern for environmental issues [113]. In periods of high-energy price volatility, improving energy efficiency is a significant approach to lower these expenses and generate predictable revenues. There are several chances for reducing energy consumption that may be accomplished at individual

iron and steel mills in an economical way. At the process, component, facility, as well as organizational levels, iron and steel industries have access to a variety of energy-efficient technologies and methods [114,115]. The most crucial areas of control for the management of the steel mill in the current situation are the reduction in energy costs and the enhancement of energy efficiency. The steel industry has achieved incredible strides in energy conservation since the 1960s, with the average energy intensity per ton of steel produced falling from 50 GJ/ton in the 1960s to its current level of roughly 20 GJ/ton. This has been accomplished by increasing the effectiveness with which various energy sources are employed, by improving the energy efficiency of the processes used in steel plants, and by making efficient use of the various materials used in the manufacture of iron and steel [114,116].

In order to achieve outcomes for energy conservation and efficiency in the iron and steel factory, effective energy management procedures are required. Energy management practices offer several opportunities in the iron and steel industry, including [111,113,117]:

- A drop in the energy intensity per ton of crude steel;
- The adoption of good energy-use practices;
- Employing effective procedures for the recovery of heat and gas energy;
- Allowing plant management to create strategies to reduce the facility's energy intensity;
- Allowing plant management to prioritize investments that will have the most impact on energy efficiency.

In addition to energy cost reductions, increased energy efficiency might have additional advantages. They consist of [111,117]:

- Reduced company risks and susceptibility to variable energy costs;
- Enhanced productivity;
- Improved product quality and a shift to market sectors with higher added value;
- Decreased environmental compliance costs.

3.1. Replacing Fossil Energy Carriers with Biomass in the Steel Industry

Coal and coke are fossil fuels that serve as the iron and steel industry's primary energy sources. One of the potential methods to minimize the use of fossil fuels and to reduce CO₂ emissions is the partial replacement of coke and coal in blast furnaces with biomass. Products made from biomass can be used in place of fossil carbon for producing metal and processing in a number of ways. As reported by Hakala et al. [67], as well as Mousa et al. [2], biomass products can be used, for instance, in [67]: partial replacement of fuel injected into the blast furnace; cokemaking for the production of bio-coke; producing bio-composites and/or bio-briquettes by pelletizing and briquetting; creating bio-sinter through the sintering process; the bio-re carburization of steel in a ladle furnace, as presented in Figure 3. The best materials for technology of bio-blast furnace are solid biomass products like torrefied wood pellets and charcoal with high calorific values as well as high content of carbon. Among other bio-products, charcoal has the largest fixed carbon content, the highest calorific value, and the least volatile matter [2].

Research performed by Mathieson et al. [118,119] concerning BF tuyere injectant replacement with pulverized coal was highlighted as the application with the most promising and biggest potential for CO₂ reduction. By lowering the blast furnace's gasification temperature and reducing the overall carbon consumption, the resultant bio-coke may be beneficial. Some ironmaking blast furnaces might cut CO₂ emissions by 15% by replacing 20% of the coke with biomass, according to estimates [120]. Even if these numbers are unlikely to be reached in the majority of situations, the size of the global steelmaking business means that even slight advancements would have a major influence. Mathieson et al. [118,119] also presented results of a typical EAF steelmaking operation's use of biomass-derived chars, which is shown in Figure 4.

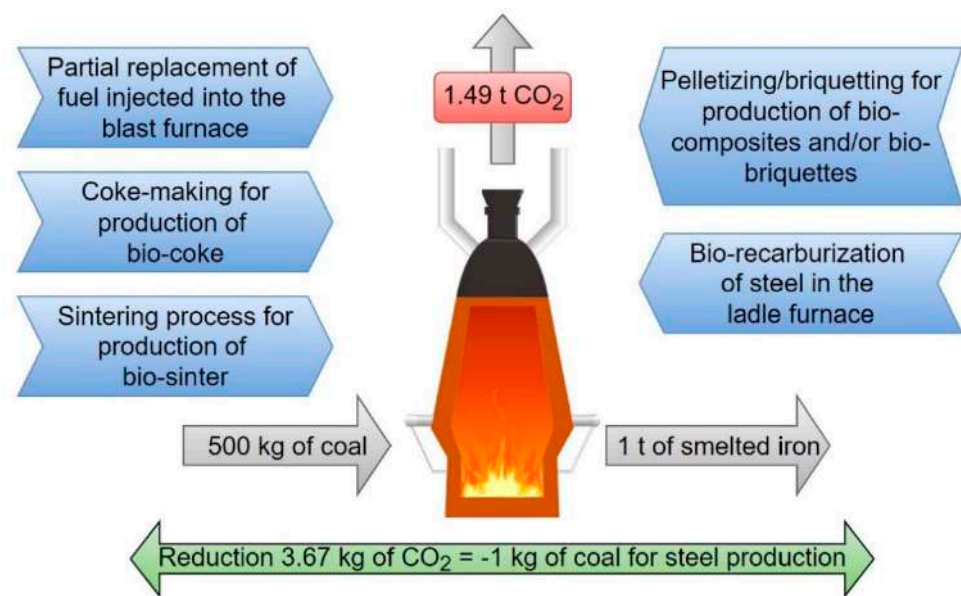


Figure 3. Main routes of replacing fossil energy carriers with biomass in the steel industry [2,67].

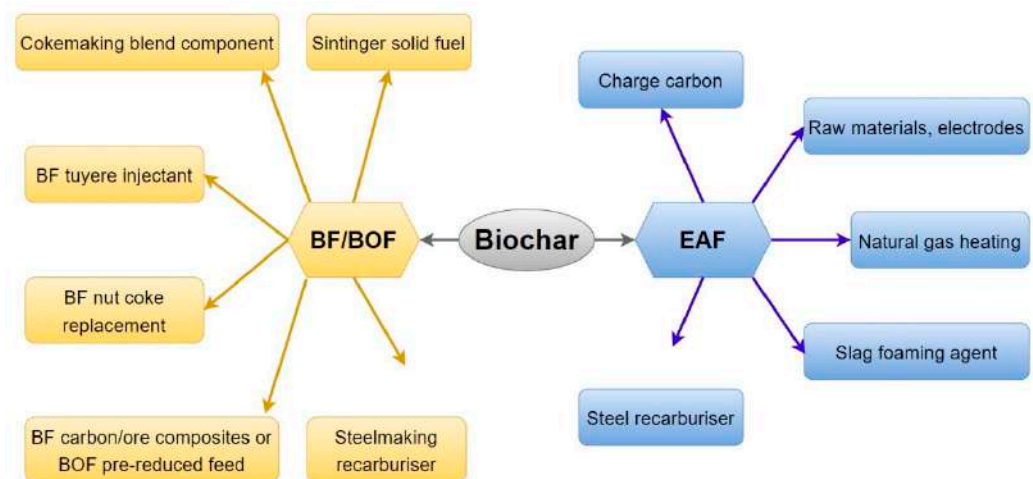


Figure 4. Applications for biochars within a typical integrated steelmaking operation and a typical EAF steelmaking operation [118].

Potentially, biochar might replace the pulverized coal that is now put directly into blast furnaces. Work has been carried out in this direction as part of the Australian CO₂ breakthrough initiative, which focused on using sustainable biochar in place of coal for pulverized coal injection (PCI) in the blast furnace. The manufacturing of charcoal is still being improved via development to increase its product criteria for steel manufacture. In the ArcelorMittal facility in Ghent, Belgium, the Torero partnership project is experimenting with using biocoal (torrefied waste wood) to partially replace coal [121]. While some blast furnaces do already run totally on biomass, these are smaller furnaces because of the relative strength of charcoal versus coke. Currently, particularly in Brazil, charcoal is utilized commercially to replace a portion of the coal applied in blast furnaces. Brazil is the global leader in production and consumption of biochar, of which approx. 75% of its production is applied in the steel industry [122,123].

3.2. Advantages of Using Biomass in the Steel/Iron Industry

Iron and steelmaking, as well as the smelting processes used to produce non-ferrous metals, both produce significant amounts of carbon dioxide (CO₂) that can be reduced by utilizing biomass as a carbon source rather than fossil fuels. Particularly this biomass, which can be recoverable from the expanding pulp industry side streams and biorefineries, might find a value-adding end application as a renewable raw material source for the metal manufacturing and processing sector [67]. With less investment and technical risk than other ground-breaking technologies in development, the use of fuels and reductants generated from biomass in the iron and steel-manufacturing industry offers a sustainable solution for lowering net CO₂ emissions. Because of its carbon neutrality, biomass cuts emissions. An efficient technique to lower GHG emissions might be to use biomass in the place of coke breeze during the sintering process. Numerous research projects have been created to lower energy usage at sintering plants; however, there has been no discernible decrease in CO₂ emissions. Researchers are focused on using biomass to reduce CO₂ emissions in the manufacture of iron and steel as a result of the ongoing release of massive amounts of CO₂ during the production of iron, which has long been a cause for worry. Biomass usage as a carbon-neutral material is an appealing approach for iron manufacture to minimize CO₂ emissions in order to address the environmental issues related to the iron and steel sectors [124]. To quantitatively assess the potential of biomass-assisted ironmaking technology to reduce CO₂ emissions, the calculation formula for energy savings and emission reduction was developed. For every ton of iron smelted, a blast furnace should burn around 500 kg of fuel and emit roughly 1.49 t of carbon dioxide. Approx. 3.67 kg of CO₂ may be reduced for every kilogram of carbon usage that is lowered. According to the calculations, the CO₂ emissions of the current blast furnace ironmaking process may be decreased by >40% if the blast furnace runs efficiently and the biomass is fully utilized in the pre-iron processes including sintering, pelletizing, coking, and injection [14]. Ng et al. [125] analyzed the effects of substituting solid biocarbon generated by torrefaction, pyrolysis (up to 900 °C), and hydrothermal treatment for coal injection. A conceptual research study using heat and mass balances together with modeling for thermodynamic equilibrium was used for further examination. They came to the conclusion that this might reduce greenhouse gas emissions by up to 20%; nevertheless, the value of using biocarbon would then be greatly influenced by its carbon-to-oxygen ratio. According to certain case studies presented in report [126], using biofuels exclusively in the place of fossil fuels can reduce steelmaking's emissions of greenhouse gas even by 25%. Other studies in the same report have estimated that using carbon-neutral biomass might lower net CO₂ emissions over the typical BF-BOF pathway by up to 58%.

In addition to being CO₂ neutral, biomass material is also probably lower in S, Cl, N, and other heavy metals, which are detrimental to the environment, human health, and metal quality [5]. The high sulfate content in coal causes SO_x emissions when it is burned. When SO_x is released into the atmosphere, it combines with water to produce acid rain, which has an adverse effect on the environment. As opposed to coal, biomass has a 10 times lower sulfur concentration. As a result, the environment is significantly cleaner. Nonetheless, the NO_x results are the same for both coal and biofuels [26].

According to the results of mathematical modeling developed by de Castro et al. [96], adding 150 kg/tHM of pulverized coal to 100 kg/tHM of charcoal will increase the efficiency of the blast furnace by about 25%, while optimizing oxygen enrichment. Another major benefit discovered by studies published to date is that biomass has a greater hydrogen concentration, which may ignite the sintering process more evenly and effectively at a lower ignition temperature.

3.3. The Challenges and Future Prospects in the Application of Lignocellulosic Biomass in the Steel and Iron Industry

In theory, metal-processing facilities might use biomass as bio-based fuel for a variety of uses. The advantages of such a method, however, are often limited owing to its low

heating value and might be offset, for instance, by the high expenses associated with preprocessing and transportation. Biomass must first be transformed into charcoals (chars) through pyrolysis or torrefaction processes since raw biomass is unsuitable for usage in the production of iron and steel [67]. On the other hand, the negative impact of biomass on the thermoplastic qualities of metallurgical coke limits the possibility of replacing coke (or even partially). A solution has not been found yet for keeping the coke bed mechanically strong in vertical shaft furnaces. This was not possible even with the introduction of small amounts of biomass, like sawdust or charcoal [120]. Even with minor (5 wt%) additions of biomaterials to the coking mix, it is predicted that the wide devolatilization range will eventually result in increased mass loss and decreased coke thermoplasticity and mechanical strength. A striking finding from other sources is that the same thermal study of Kraft lignin from softwood (pine or spruce) reveals minimal to no secondary devolatilization ranges [127]. Since pulverized coal injection (PCI) can already contain some amounts of nut coke or charcoal, replacing it represents the technically easier choice [2]. Similar environmental advantages to using bio-coke will result from the injection of charcoal, which will take the place of tuyere oil or coal injection. Additionally, it has been said that the use of biochar will boost reactivity and aid in reducing slag and ash production during smelting processes [128].

In the iron and steel sector, there are numerous distinct pyrometallurgical processes. As a result, the process itself and the function of the carbon material in the process determine the requirements for the qualities of carbon material. The BF processes have the strictest criteria for the characteristics of the carbon material because metallurgical coke plays a crucial role in maintaining the process' permeability and carburizing the iron. It is also being utilized as a reductant and a source of heat. As a result, severe criteria are placed on the qualities of carbon material, including mechanical strength, reactivity, and density. Other pyrometallurgical processes may have less stringent criteria, but they all require materials to have the same crucial qualities, such mechanical strength, reactivity, and apparent density [129]. When pyrometallurgical operations use biocarbon instead of carbon derived from fossil fuels, there are several difficulties. The enormous surface area and very porous structure of biocarbon cause an unfavorable increase in CO₂ gasification reactivity [130]. However, according to Koskela et al. [131], pyrolysis temperature as well as briquetting, i.e., agglomeration, can change the gasification reactivity of biocarbon. The structural features of biocarbon are changed by high pyrolysis temperatures and briquetting which result in a denser and smaller surface area. This is connected to the selection of the raw material and its lignin content for the production of biocarbon. This is because lignin possesses an adhesive quality, which enhances the binding of the particles during briquetting. According to research performed by Wiklund et al. [132] as well as Helle et al. [133] and Babich et al. [74], the pyrolysis temperature also has a significant impact on the biomass composition, calorific value, and output yield. In these works, with the example of Norway spruce, the content of hydrogen, oxygen, carbon, as well as the calorific value and yield depending on the pyrolysis temperature, were analyzed. However, in the temperature range up to 500 °C, the observed changes in these parameters were the greatest, and at temperatures between 600 and 800 °C, both the composition and the calorific value differed slightly.

Biomass addition to the coal blend used to make coke has recently been the subject of intense research. Operating a blast furnace (BF) requires the use of carbon-bearing materials, and the standards are stringent. CRI and CSR are two of the most crucial factors in determining whether to use metallurgical coke in a BF. The industrial quality standards for coke are a CRI—coke reactivity index—under 30% and a CSR—coke strength after reactivity—above 55%, while in European countries, the CRI and CSR standards in BFs are 23% and 65%, respectively [128]. According to Safarian et al. [134], the maximum quantity of biochar that may be blended with coal in order to make bio-coke of a high enough quality greatly depends on three indications of fluidity as well as CSR and CRI. The findings demonstrated by them showed that adding charcoal often causes the fluidity

of the coal–biochar mixture to diminish. The CRI, CSR, and fluidity indices of the coke decrease when biochar is added to coking coal, and biochar has a detrimental impact on the quality of the output coke. It was discovered that in order to prevent negative effects on the quality of the resultant coke, biochar must be added continuously at a rate of between 2 and 10% during the coke-making process. Adding 2 to 10% biochar to the coal mix decreases CO₂ emissions in the steel sector by 1–5%, which is valued at 0.02–0.11 tons of CO₂/ton of crude steel. The CSR and CRI of the coke also fall, although fluidity marginally improves as a result of lowering the particle size of the biochar. A range of 2–4 mm was determined to be the ideal particle size for biochar [135].

In turn, the results of research performed by Yustanti et al. [136] showed that two analyzed coking blends of coke with biochar from coconut shells as well as rice husks generated comparable tendencies. The coke quality blends degraded as the biochar proportion rise, i.e., from 0 to 25 wt%, as shown by the CSR index decreasing and the CRI index increasing in the case of both biomass species. For the analyzed biochar proportion of blends of coke with rice husks, the CSR index was from 62.7% to 24.5% and in the case of coconut shells, was from 62.7% to 42.6%. In turn, the CRI index was rising in case of blend of coke with rice husks from 21.3% to 47.3% and in case of coconut shells from 21.3% to 32.9%. Thus, in order to maintain good-quality coke, the CRI index should be, if possible, the lowest, while the CSR index should be the highest.

An interesting study was presented by Gul et al. [137], who proposed using cutting-edge techniques to make biocarbon on the route of pelletization of charcoal with pyrolysis oils and then reheating it at conditions of high temperatures in order to generate materials characterized by sufficient hardness, decreased porosity, and appropriate reactivity. After such pretreatment, biocarbon can meet the standards typically required for metallurgical coke. A technological, economic, and environmental study of the anticipated end application of biocarbon in the steel and silicon industries was provided. Based on their research, the use of biocarbon pellet in the steel industry will undoubtedly have some positive environmental effects. The cost of the feedstock, shipping expenses, cost of the transformation, and expenditures of the pyrolysis plant are just a few of the numerous variables that will determine the economic viability. According to Hakala et al. [67], the cost of producing one tonne of biochar might be 252 euros, which is the lowest calculated price that can be obtained. The price of the EU Emission Trade System, especially EUA entitles businesses to release GHGs with a global warming potential equal to one tonne of CO₂ equivalent, and the price of coke will both have an impact on the eventual profitability of the biocarbon use in the steel sector. According to Gul et al. [137], it is challenging to have an economic convenience when the EUA costs 25 EUR /tCO₂, unless coke costs more than 200 EUR /t. In the global market, it is quite challenging to achieve this value. The material's quality must, thus, be improved in order to achieve the same qualities as coke, even if some economic factors still need to be optimized, primarily focused on technology and raw material cost reduction. As a result, the created biocarbon pellet has to be examined in accordance with all the usual standards used to describe coke, including the ISO 18894:2018.

According to Fan et al. [126], the actual use of biomass is severely constrained, and there are still considerable technological barriers preventing its full replacement of fossil fuels in the BF-BOF process, including, first of all, the cost. Currently, the price of biocharcoal ranges from USD295 to USD525 per ton, while the price of coke (coal that has undergone the coking process) is around USD200 per ton. Purely economically, biomass cannot yet compete with coal. Secondly, another barrier is the physical characteristics. Biocharcoal differs from coal or coke in terms of physical characteristics (such as mechanical strength, etc.), and manufacturing performance criteria may not be guaranteed. The qualities of bio-coke that is used to directly replace coke in BF must be comparable to those of regular coal. Furthermore, Gaurav Jha et al. [26] listed the qualities being necessary for any fuel used in metallurgical operations that should be primarily profitable from the perspectives of availability, storage, acceptability, etc. The biochar ought to be characterized by: high heating value and energy density; low ash and moisture content; low levels of

pollution and impurities; easy and abundant availability; reasonable price; ease to transport; flame resistance in an open space. Thirdly, another barrier is the supply chain quality. The worldwide supply networks are immature and sometimes poorly managed, and biomass resources are allocated unevenly. Brazil is the world's top producer of biochar, followed by China, India, and the United States. Bio-charcoal might legitimately service a small portion of the steel industry in such areas. Contrarily, the EU now imports 70% of its bio-charcoal from Africa, which has increased worries about deforestation, biodiversity loss, and eco-colonialism. Similar worries are raised by the absence of indigenous biomass supplies in Japan and Korea [126].

- The use of biomass in the iron and steel sector is currently rather restricted, and it faces stiff competition from traditional fossil fuels. Technical and financial issues that call for cooperation between the steel industry and the bioenergy sector are among the difficulties associated with using biomass in the steel industry. Although a significant effort has been made up to this point, there is still long way to industrial application of biomass in iron and steel sector on the wide scale. A peculiarity of Brazil in comparison to other countries consists of the fact that its main energy sources for steel production are coal, electricity, and charcoal obtained from biomass. The example of Brazil, which is one of the biggest steel producers in the world, shows that application of lignocellulosic biomass in steel sector can be possible not only on a pilot scale but also on a wider, industrial scale [138,139].
- According to a report presented by ArcelorMittal [140] in 2018, the company started a EUR 40 million Torero demonstration project in Belgium (Ghent) using 120,000 tonnes of waste wood to create bio-coal that may be used in place of fossil fuels to reduce iron ore. The technique may be able to handle a range of waste streams (such as bio-based and plastic waste) produced by society.

4. Summary and Conclusions

Among all industrial sectors, the iron and steel industry is the largest energy user. Coal, liquid and gaseous fuels, and electricity are the primary energy sources in this energy-intensive sector of the economy. The iron and steel industry places a high priority on energy because of the high energy intensity and the significant contribution of fossil fuels. Additionally, the steel and iron industries are subject to rivalry on a global scale, and producing steel using less energy may provide them an edge. The usage of fossil carbon is presently a major component of the metal manufacturing and processing business. Both the smelting reduction required to produce pure metal from ores and the energy supply for the subsequent processing steps, where heavy mineral oils are typically utilized, depend on coal and coke. With 4–7% of worldwide emissions and a comparable range in European emissions, the production of iron and steel is among the top industrial carbon dioxide emitters. This paper examined the idea, scientific theories, and research in the field of biomass application in metallurgy as a replacement of coal.

Clearly, there is still a long way to go before biomass materials are widely used in metallurgical sectors. First, biomass materials must attain properties that are best suited for their future uses, such as the sintering of iron ore and the production of iron in blast furnaces. The cost and accessibility of biomass materials must also be taken into account, in addition to their appropriateness for metallurgical applications in terms of quality. Two significant barriers to the adoption of biomass materials in metallurgical industries are their cost and availability. There is an urgent need for more study on the production chain and availability of biomass resources for metallurgical purposes. Also, actions in the development and management of the use of biomass in a sustainable manner and to enhance a production technology with high efficiency, low cost, and lower environmental impact should be taken.

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Article

Possibilities of RDF Pyrolysis Products Utilization in the Face of the Energy Crisis

Magdalena Skrzyniarz ¹, Marcin Sajdak ^{2,*}, Monika Zajemska ¹, Anna Biniek-Poskart ³, Józef Iwaszko ¹
and Andrzej Skibiński ³

¹ Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology, 19 Armii Krajowej Ave., 42-200 Czestochowa, Poland; monika.zajemska@pcz.pl (M.Z.)

² Center of New Technologies, Department of Air Protection, Faculty of Energy and Environmental Engineering, Silesian University of Technology, 22 B Konarskiego Ave., 44-100 Gliwice, Poland

³ Faculty of Management, Czestochowa University of Technology, 19 B Armii Krajowej Ave., 42-200 Czestochowa, Poland; anna.poskart@pcz.pl (A.B.-P.)

* Correspondence: marcin.sajdak@polsl.pl; Tel.: +48-32-237-15-19

Abstract: The main goal of the study was to assess the possibility of practical use of products of pyrolysis of refuse-derived fuel (RDF), i.e., pyrolysis gas, biochar and pyrolysis oil, as an alternative to standard fossil fuels. The subject matter of the paper reaches out to the challenges faced by the global economy, not only in the context of the energy crisis, but also in the context of the energy transformation currently beginning in Europe. The increase in fuel and energy prices prompts countries to look for alternative solutions to Russian minerals. At the same time, the growing amount of municipal waste forces the implementation of solutions based on energy recovery (the amount of municipal waste per EU inhabitant in 2021 is 530 kg). One such solution is pyrolysis of RDF, i.e., fuels produced from the over-sieve fraction of municipal waste. In Poland, insufficient processing capacity of thermal waste conversion plants has led to significant surpluses of RDF (1.2 million Mg of undeveloped RDF in Poland in 2021). RDF, due to their high calorific value, can be a valuable energy resource (16–18 MJ/k). This issue is analyzed in this study.

Keywords: RDF; pyrolysis; steel and iron industry; sustainable production; energy crisis



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1. Introduction

The energy crisis that is currently affecting many countries around the world is largely due to the global economy's dependence on non-renewable fossil fuels such as coal, oil and natural gas [1]. Rising energy prices have contributed to the rising inflation, forcing some industrial plants to reduce or even stop production. Energy costs have also slowed down economic growth to such an extent that some countries are now heading for a deep recession. Production in Europe in particular, which consumes large amounts of gas in production processes, has suffered the most. These plants were forced to reduce their output because they could not afford to continue operating.

In addition to the energy crisis, the management of municipal solid waste is currently one of the biggest challenges, especially with regards to the environment [2]. The amount of municipal solid waste is increasing day by day all over the world [3] due to the continuous growth of industrialization, urbanization, consumerism, population growth and other factors [4]. Improper waste management has a negative impact on the environment [5], contributes to an increase in the amount of methane emitted into the atmosphere (which is one of the main factors responsible for global warming), causes deterioration of water quality and soil properties, and adversely affects human health [6]. Literature data show that since 2004 the world's largest producer of municipal solid waste (MSW) is China, which in one year collected six billion tons of unprocessed MSW in about 200 out of the 660 metropolises of the country. Improper management of MSW not only has a negative impact

on the environment, but also poses a threat to public health and raises other socio-economic problems. Waste-to-energy (WtE) technologies such as pyrolysis, gasification, incineration and biomethanization [7] can convert MSW into usable energy (electricity and heat) in a safe and environmentally friendly way [8].

The results of literature research clearly prove that pyrolysis of municipal waste is a valuable source of secondary fuels, the wider use of which will contribute to further reducing the amount of landfilled waste, while increasing the diversification of fuel and energy sources in Poland [9,10].

On a national scale, it is not possible to convert all waste into RDF and, consequently, it is not possible to use them to the maximum extent in terms of energy [11]. An alternative to an incineration plant may be pyrolysis and waste gasification technology producing gas, the composition of which depends not only on the conditions of the process, but above all on the type of waste incinerated [12]. At present, the most problematic group of waste in terms of thermal conversion is plastic [13], rubber [14] and textile [14] waste. Spent railroad sleepers are also noteworthy, impregnated with creosote oil containing, among others, anthracene, fluorene, phenanthrene, benzo(a)anthracene and benzo(a)pyrene [15]. In addition to hydrogen, carbon monoxide and a small amount of methane, polycyclic aromatic hydrocarbons (PAHs) (Table 1) are also present in the composition of gas obtained as a result of thermal conversion of waste. The chemical composition of both pyrolysis gas and gas from waste gasification can be highly diverse, which translates into the impact of their combustion on the environment [16].

Table 1. PAH contents in the gaseous product after thermal conversion of municipal solid waste (MSW) and municipal solid waste co-incinerated with coal (MSW/Coal) in µg/g [16].

PAHs	Process Temperature									
	500 °C	600 °C		700 °C		800 °C		900 °C		
	MSW	MSW/Coal	MSW	MSW/Coal	MSW	MSW/Coal	MSW	MSW/Coal	MSW	MSW/Coal
2-ring	57.3	21.3	184.0	41.2	288.1	44.4	43.42	22.73	400.0	25.2
3-ring	671.8	67.26	1221.6	108.1	4283.7	257.9	5619.3	285.2	3078.9	884.5
4-ring	225.5	5.30	783.8	9.6	4040.6	15.2	1110.2	9.2	2002.3	1132.5
5-ring	14.4	0.52	98.9	0.2	835.4	4.9	100.1	0.1	235.8	70.9
6-ring	3.36	0.06	30.6	0.0	201.2	2.0	0.4	0.1	119.1	37.5
Sum	972.4	94.60	2319.0	159.2	9649.1	324.5	6873.4	317.5	5836.2	2150.8

Due to the energy crisis, many industries, including the iron and steel sectors, are facing economic problems and a loss of competitive advantage [17]. In connection with the above, numerous efforts are being made to increase energy efficiency of the metallurgical industry and thus reduce production costs, through, inter alia, the use of waste energy and alternative fuels (Figure 1) [18,19].

As revealed by literature sources, the iron and steel industries have great potential and opportunities to increase their energy efficiency, reduce carbon dioxide emissions and, as a result, promote sustainable development by replacing conventional fuels used in metallurgical processes with alternative fuels, including biomass (Figure 2) [20].

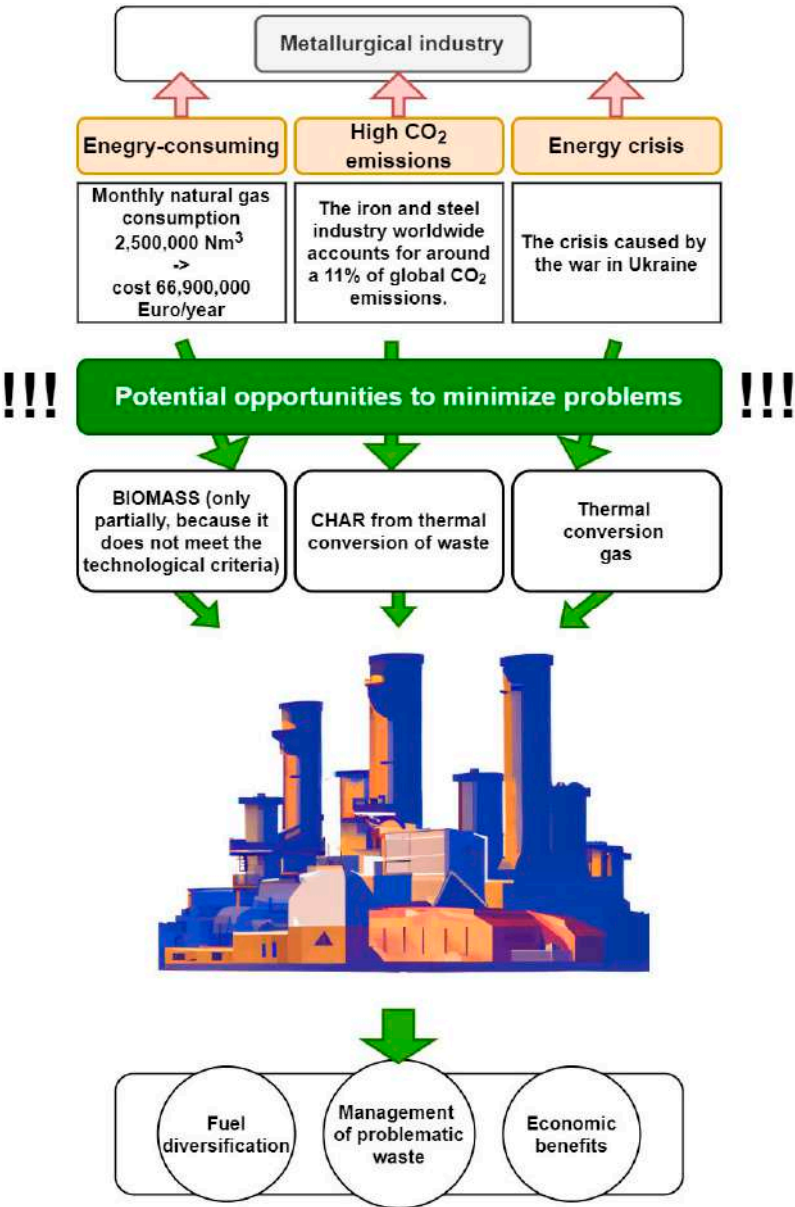


Figure 1. Potential opportunities to improve energy efficiency of the metallurgical industry [20].

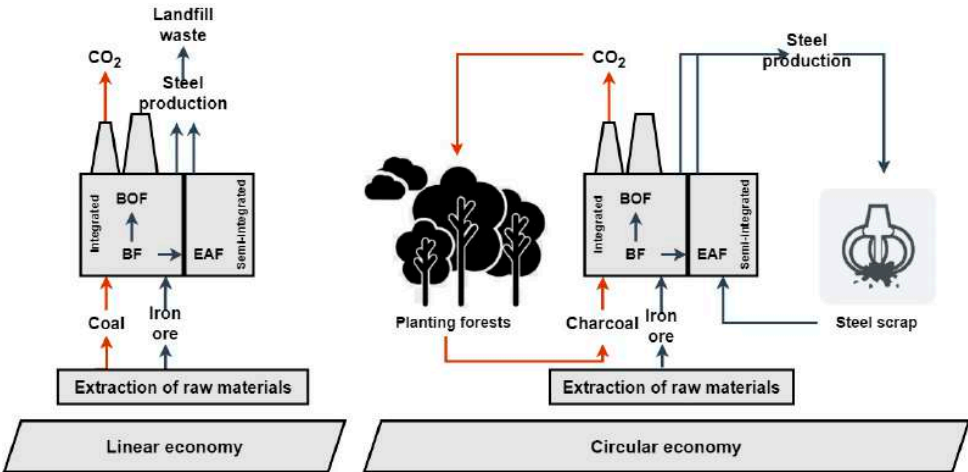


Figure 2. The idea of linear and circular economy in the metallurgical sector [8].

2. Theoretical Background

2.1. Energy Potential of RDF

RDF is a type of alternative fuel produced from MSW. Their calorific value is estimated at about 16–18 MJ/kg [21]. The process of producing RDF consists of separating combustible substances (rubber, paper, plastics, wood, etc.) from the municipal waste stream by sorting [10]. Thanks to pelletization, RDF is characterized by a homogeneous particle size, but the diverse composition of these fuels may cause high variability of their physico-chemical properties. It is worth noting, however, that the Polish waste segregation system primarily uses mechanical-biological waste treatment plants, thanks to which adverse variability of the composition is reduced and a good input material for the production of RDF is obtained. The fraction selectively separated from the solid waste stream is characterized by increased stability of the material composition, and the impact of the waste collection site is negligible (Figure 3) [22,23].

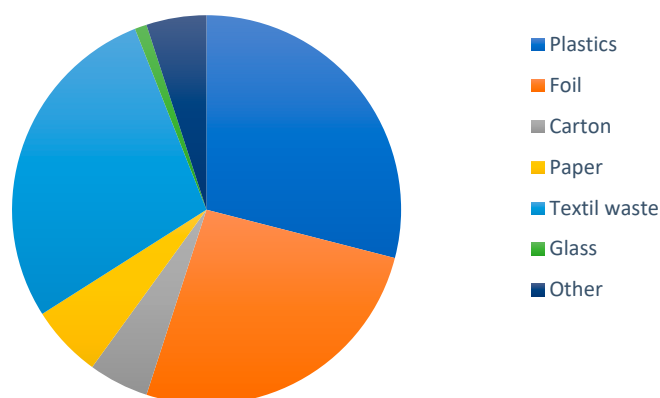


Figure 3. Typical composition of alternative fuels produced from mixed municipal waste in Poland [24].

Research by the authors of the publication [24] showed that the composition of 12 samples of alternative fuels was dominated by combustible components, such as plastics, wood, textiles, paper and cardboard, which together accounted for 94% of the mass of RDF. Other components found in the fuels were non-flammable and their presence negatively affected the calorific value of RDF. Producers and consumers of alternative fuels want the non-flammable fraction to constitute the lowest possible percentage of the fuel mass. This fraction should not be present in the alternative fuel, but often contaminates it as a result of bonding with other waste [24]. For comparison, Figure 4 shows the composition of solid recovered fuel (SRF)/refuse-derived fuel (RDF) in selected European countries. Composition studies were conducted between 2009 and 2019 and the results were averaged for all the countries [25]. Differences in the composition of fuels produced from waste may result from different waste management models in the individual countries. The culture and the ways of disposing of waste can also have an impact, as well as, for example, the way products are packed and the type of material used for this purpose.

2.2. Legal Background of Energy Recovery from RDF

Thanks to the departure in the EU from the linear economy model to the circular economy (CE) and the implementation of the “zero waste” idea, all of the EU countries are striving to stop landfilling municipal waste [26]. Changes in waste management are expected to have a beneficial impact on the economy, the environment and the health of residents of EU countries. One of the main documents introducing changes in waste management is the “Circular Economy Package” (2015), which implements long-term measures to reduce landfilling and to increase the reuse and recycling of waste [27].

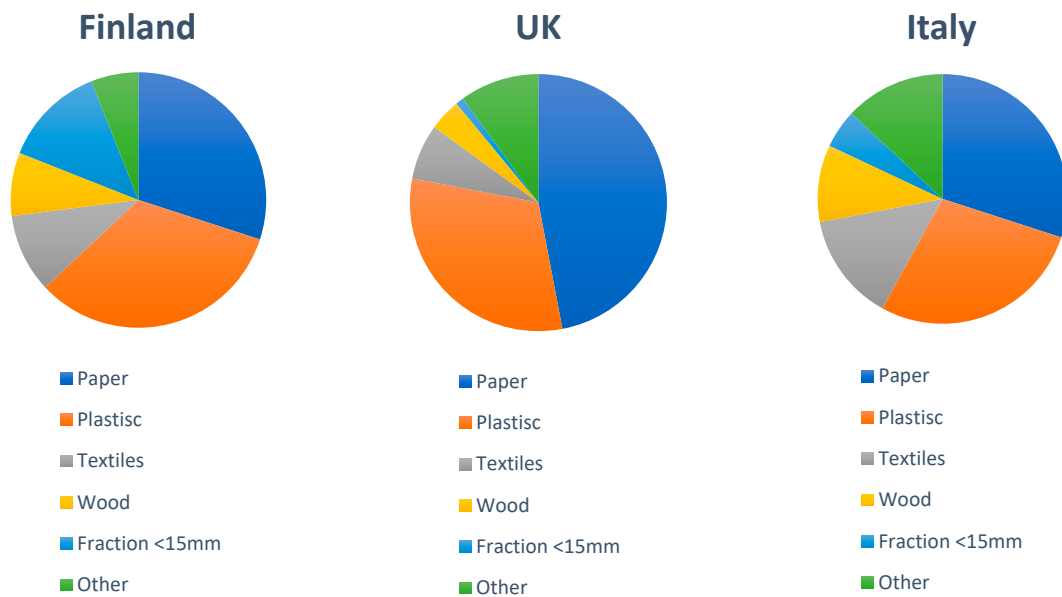


Figure 4. Typical compositions of samples of SRF/RDF commercially produced from municipal solid waste (Finland, UK, Italy) [25].

In Poland, appropriate legislative measures were also taken, convergent with the EU legislation and with the Regulation of the Minister of Economy (in force since 1 January 2016) which prohibit, among other things, the landfilling of high-calorific waste, i.e., waste with a combustion heat above 6 MJ/kg of dry matter (Figure 5) [28]. Although legal solutions to minimize the problem of waste storage have already been introduced and are in force, RDF have not obtained the status of “fuels” yet. These materials are still categorized as waste identified with code “19 12 10”. Additionally, until now, neither the EU nor the Polish legislator has clearly defined what parameters RDF should have [29]. The lack of top-down unification of RDF parameters results in great freedom in determining the requirements of various industries or enterprises regarding these fuels. For example, the main clients for RDF (cement plants) approach these requirements very rigorously, setting fuel specifications at a very high level (Table 2).

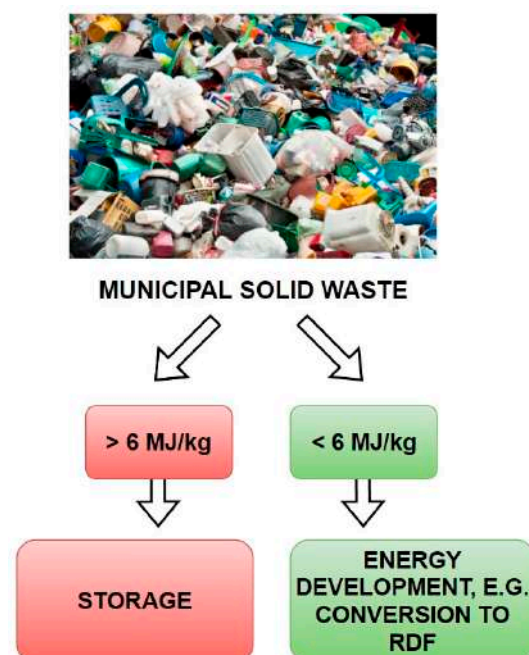


Figure 5. Waste management in terms of calorific value [24,28,29].

Table 2. Required specifications of RDF (19 December 2010), ODRA S.A. cement plant.

Parameters	Units	Acceptable Limits Values
Total moisture content	%	≤18.0
Total sulfur content (operating condition)	%	≤0.5
Chlorine content (dry state)	%	≤0.7
LHV (operating condition)	GJ/Mg	≥20.0

Taking into account the amount of municipal waste produced each year in Poland (about 13.7 million tons, year 2021), the part suitable for thermal conversion accounts for 21.5% (2.7 million tons) (GUS data source). Cement plants burn only about 1 million tons per year (very restrictive calorific value standards > 18–20 MJ/kg), which means that other consumers, for example heating plants, are unable to consume all the fuel that is produced [24]. The constant increase in the amount of municipal waste also causes an increase in the production of fuel from waste. The need to manage the newly created waste fuel may be noticed in the extraction of fossil fuels, which in turn will have an impact on the climate and energy economy [30].

2.3. Processes of Thermal Conversion of Municipal Waste

In order to prioritise environmental concerns, European legislation mandates Member States to adhere to progressively rigorous rules pertaining to waste management and the mitigation of pollutant emissions. The objective of this initiative is to reduce the amount of trash that is disposed in landfills by promoting the utilisation of thermal waste conversion techniques for the recovery of materials and energy [31]. Thermochemical conversion methods like as pyrolysis and gasification have been found to result in reduced emissions of pollutants into the atmosphere as compared to combustion [32]. Moreover, these methods are considered economically feasible for the treatment of municipal or industrial waste. In recent years, there has been a growing recognition of the significance of pyrolysis and gasification techniques in mitigating the environmental consequences associated with combustion processes and the generation of power from waste materials. The employment of these methodologies facilitates significant adaptability in the utilisation of primary resources and also facilitates the acquisition of chemical energy in the shape of hydrocarbon products, alongside electrical power. The widespread adoption of waste-to-energy technology has the potential to reduce reliance on fossil fuels. According to a study conducted in the United States [33], the substitution of 0.4 tons of coal used for electricity production can be achieved by recovering each ton of municipal waste. It is anticipated that the widespread use of these technologies in the United States will result in a significant decrease in coal consumption, estimated to be approximately 100 tons year [33].

The circular economy model incorporates the utilisation of energy derived from trash, resulting in the neutralisation of the energy balance for several waste materials. The utilisation of the latent energy present in waste materials should be harnessed in order to fulfil energy demands, specifically for the generation of heat and electricity. The economic and environmental justification for harnessing the potential of garbage has been documented [34].

It is important to acknowledge that, in accordance with the relevant waste management hierarchy, the process of energy recovery takes precedence above recycling and composting. Hence, it is imperative to take into account the categorization of trash that is neither economically viable or technically unfeasible for recycling and composting (as seen in Figure 6) [26,35,36].

To release energy stored in waste, various methods of thermal conversion are used: incineration, pyrolysis, torrefaction and gasification (Figure 7) [37].

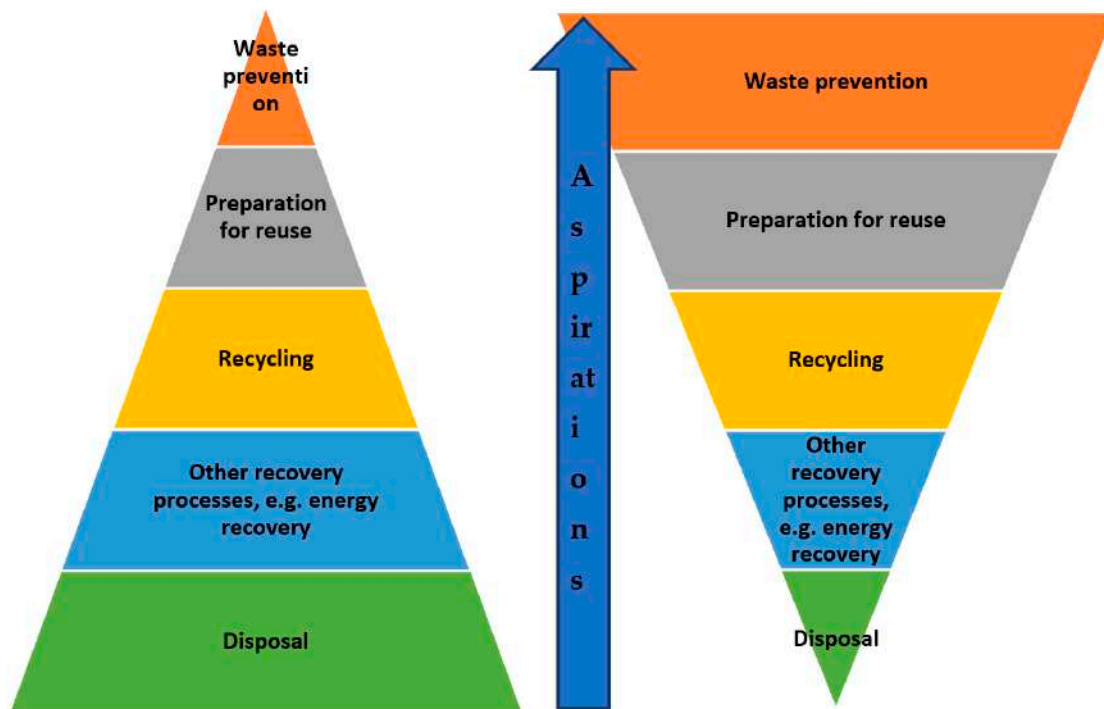


Figure 6. Waste management hierarchy [28].

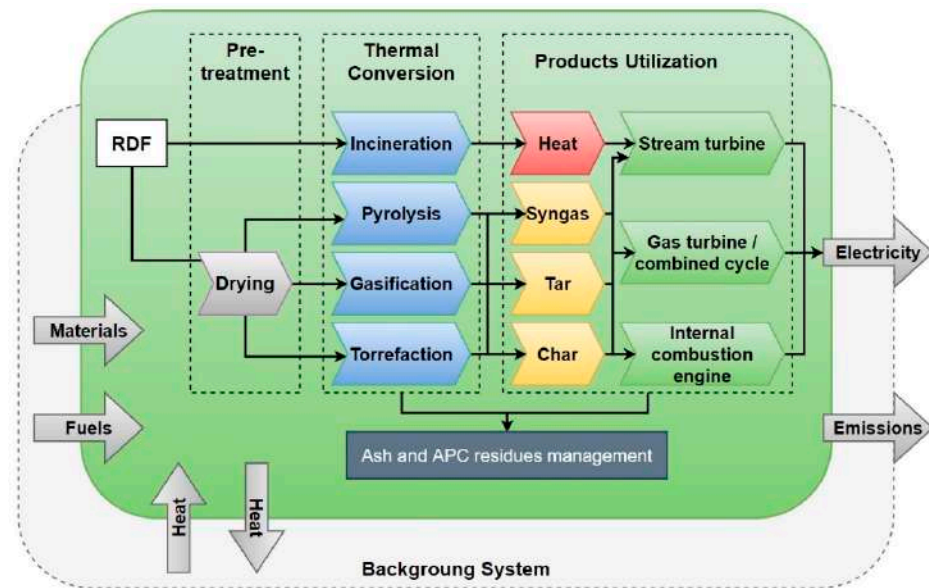


Figure 7. Methods of thermal conversion of waste [38].

The thermal conversion techniques depicted in Figure 7 are employed globally in diverse combined heat and power facilities to generate both electricity and heat [27]. However, it is important to note that each of these processes exhibits variations in parameters, including atmospheric conditions (namely the presence of oxygen), operating temperature, reactor system, and other factors. The assessment of end products and intermediate products is conducted to ascertain their quality. The temperature of a thermal process is mostly influenced by the appropriate design of the plant, the kind of reactor, and the input materials [39,40]. In underdeveloped nations, the practise of pre-treating trash is typically not observed in the context of incineration, as untreated municipal waste is commonly utilised as a primary input. Tables 3–6 in the cited literature [9,41–44] provide a comprehensive analysis and comparison of the various approaches employed for the thermal

conversion of waste. Without a doubt, combustion is the prevailing mechanism of thermal conversion [45]. The technique described is well recognised and may be easily initiated and implemented in various regions, thanks to the prevalence of technology and the existence of ubiquitous infrastructure [27]. Nevertheless, combustion has numerous drawbacks in comparison to pyrolysis or gasification techniques [46].

Tables 3–6 present a comparative analysis of the primary benefits and drawbacks associated with pyrolysis and gasification methods, as indicated by reference [47].

Table 3. Comparison of advantages and disadvantages of the pyrolysis process [48–50].

PYROLYSIS	
✓	✗
• The sole thermochemical process capable of producing liquid, solid, and gaseous fractions suitable for immediate utilisation in diverse power plants; • A process with high flexibility, ability to control parameters (temperature, pressure, dwell time) so as to obtain the desired product; • Complete destruction of toxins (furans and dioxins); • The process is suitable for the disposal of many types of plastics and other waste groups; • Environmentally friendly—low NO_x and CO₂ emissions; • Less exhaust gas; • [Higher efficiency of energy recovery from] waste compared to other methods of disposal; • Energy recovery rate of up to 80%.	✗ High initial investment costs; ✗ The need for fuel with a high calorific value is driven by the necessity for processed waste, particularly plastics, to possess a high calorific value in order to ensure the quality of the secondary fuels derived from them; ✗ High water content in liquid oily products; ✗ Technology little known to the “average person”, which raises concerns about its use.

Table 4. Comparison of advantages and disadvantages of the gasification process [41,48,49,51].

GASIFICATION	
✓	✗
✓ High energy efficiency of the process and reduction of pollutant emissions; ✓ The resulting syngas is easy to purify compared to flue gas treatment after conventional waste incineration; ✓ Waste gasification technologies using cogeneration systems based on reciprocating engines enable their use in existing waste management systems; ✓ Reduction of waste volume by up to 95%; ✓ The possibility of using the method to manage various groups of waste.	✗ Tar production; ✗ High initial investment costs; ✗ Poor availability of infrastructure with reactors for waste gasification; ✗ Corrosion of metal pipes during reaction; ✗ Higher power consumption; ✗ The amount and composition of syngas from gasification depending on the type of waste, gasifying agent, temperature, pressure and method of gasification.

Table 5. Comparison of the benefits and drawbacks of the torrefaction process [52–54].

TORREFACTION	
✓	✗
✓ Torrefaction products are biochar and torgas, ✓ Torrefied raw material has very low moisture (1–6%), higher calorific value and energy density, better abrasion and more uniform characteristics, lowering waste volume by 30% and keeping up to 90% of the basic energy in biochar, ✓ The possibility of using the method to manage various groups of waste, ✓ Torgas produced can be used to dry torrefied waste/fuel (torgas contains around 10% of the energy present in the initial material), ✓ Financial analyses encourage the construction of heating plants adapted to torrefied RDF combustion, showing high return on investment.	✗ The torrefaction technology has not yet reached commercial status and is still at the stage of research and testing in pilot installations, ✗ High ash content in the fuel, ✗ High initial investment outlays,

Table 6. Comparison of advantages and disadvantages of the combustion process [55–57].

COMBUSTION	
✓	✗
✓ Technology widely known and used on a massive scale, high availability of boilers and infrastructure, ✓ The technological process does not raise objections from society due to its universality, ✓ Combustion reduces up to 90% of the volume of the burned material.	✗ Combustion releases carcinogenic compounds such as dioxins and furans, as well as increases the emissivity of greenhouse gases and other air and atmosphere pollutants., ✗ The need to adapt an expensive exhaust gas treatment system, ✗ The greatest source of low emission is heat production (the combustion of low-quality fuels in boilers). ✗ Combustion wastes resources whose re-use saves more energy and reduces the amount of pollution generated, ✗ High initial investment outlays, ✗ Highly energy-intensive process.

The concept underlying the pyrolysis process is the heat decomposition of organic matter [58], specifically in the case of refuse-derived fuel (RDF), in the absence of oxygen. This process yields gaseous, liquid, and solid byproducts (Figure 8) [59].

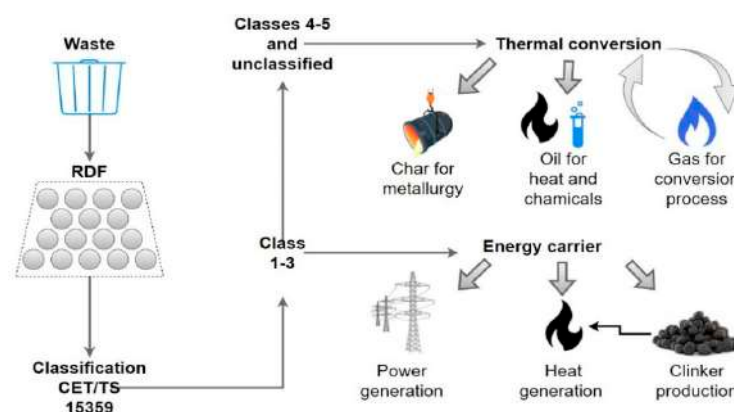


Figure 8. Diagram of the RDF pyrolysis process [60].

3. Possibilities of Using RDF Pyrolysis Products

Today, both Polish and global heavy industry (including the power generation sector) is characterized by high energy intensity, in addition to high pollutant emissions [42]. Given that improving energy efficiency is one of the priorities of the EU's energy policy, particular emphasis is placed on all forms of fuel and energy saving [61]. When it comes to Poland, there are many opportunities to save energy with relatively small financial resources. One solution is to use pyrolysis gas from the thermal conversion of RDF to fire metallurgical furnaces without the need for their pre-treatment, which in the case of polycyclic aromatic hydrocarbons (PAHs) is extremely problematic and expensive [16,62,63].

The issue of management of RDF pyrolysis products deserves attention, as evidenced by the interest of both waste management and metallurgical companies, among others, due to the following [64,65]:

- The possibility of managing the surplus RDF;
- The possibility of managing environmentally harmful plastic waste, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) [66], textile and rubber wastes, as well as gaseous products of thermal conversion of these wastes;
- The possibility of reducing the consumption of natural gas for heating furnaces, which will translate into economic benefits [20,67].

The products of RDF pyrolysis are currently used mainly for energy generation purposes (Figure 9) [46].

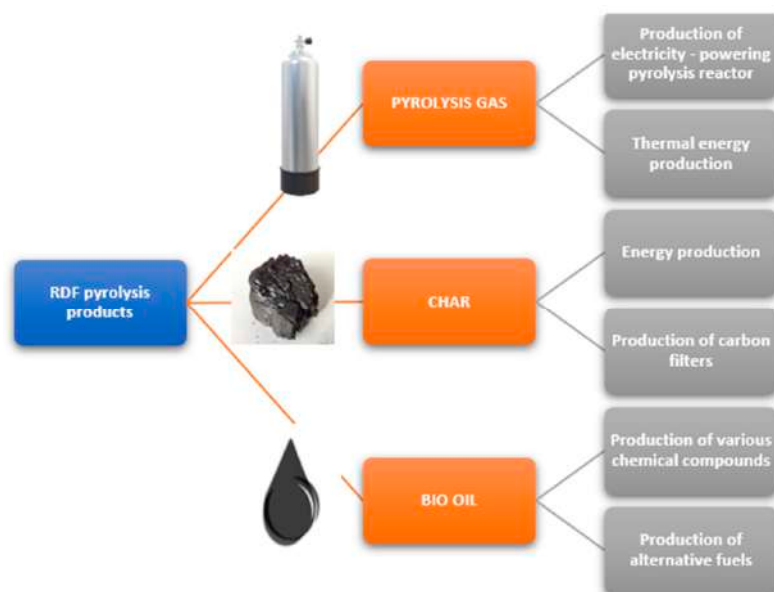


Figure 9. Uses of RDF pyrolysis products [24,24,62,68–70].

The gas fraction produced at higher temperatures, without a catalyst, is characterized by a high calorific value of about 28 MJ/m^3 . So high calorific value makes this gas an attractive fuel which can be used not only in industrial boilers, but also in gas engines and turbines, enabling the production of electricity and heat [71]. At the same time, gas obtained after the catalytic process can be used to produce methanol, hydrocarbons, ammonia or liquid fuels by Fischer–Tropsch synthesis. Pyrolysis gas may also be a potential source of hydrogen due to its significant content [72]. This aspect can have a significant impact on the environment, as about 95% of H_2 comes from fossil fuels, and the share of this product in the energy market is increasing due to the growing demand for zero fuel emissions. Therefore, hydrogen obtained in this way can play an important role in the petrochemical, electronic, metallurgical and transportation industries. In addition, mention should be made of the potential use of pyrolysis gas as a fuel in integrated gasification combined cycle (IGCC) boilers, where its environmentally friendly nature could contribute to reducing the cost of gas purging equipment [73,74].

Biochar and pyrolysis oil can be used as energy raw materials or as base substances for the production of various chemicals [75–77]. Oil produced by RDF pyrolysis can be a good base for the production of substances such as styrene, benzene, toluene, xylenes (BTX) and naphthalene derivatives [24,60,69–71]. Biochar, which is a solid carbonized product of thermochemical conversion of municipal waste, is currently a popular alternative to expensive activated carbon due to its properties, especially in adsorption applications [42]. At the same time, this solid product from the pyrolysis of municipal waste can be a valuable fuel due to its relatively high calorific value ($18\text{--}30 \text{ MJ/kg}$) (Figure 10) [42,78].

Taking into account the calorific values (Figure 10) featured by the individual RDF pyrolysis products, it can be seen that this factor determines their use in the industry [10,74,75]. The energy crisis caused by the armed conflict between Russia and Ukraine, the increase in fuel prices and the diversification of fuel suppliers are very important factors that affect the management of pyrolysis gas, biochar and bio-oil [76].

The products of pyrolysis vary in calorific value and composition due to different parameters [79], including feedstock type, reactor system, gas dwell time, heating rate, exposure time, temperature, pressure ranges, catalyst activity (if any), and the presence of hydrogen gas or hydrogen compounds [80].

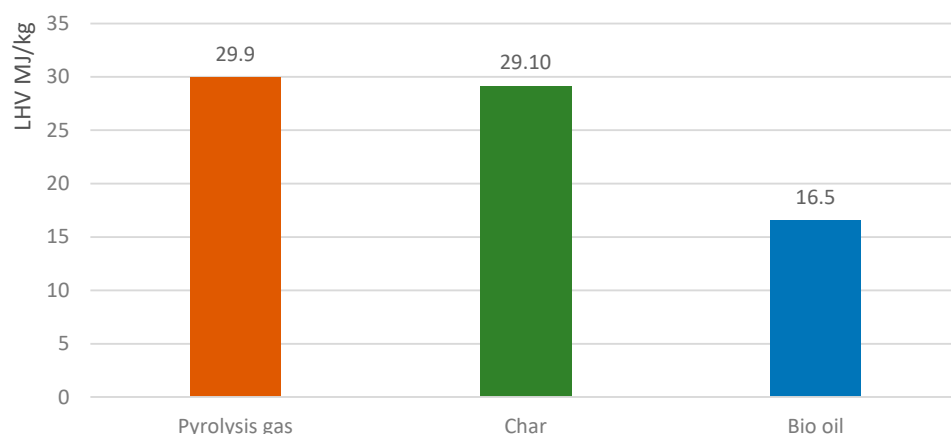


Figure 10. Comparison of calorific values of the individual RDF pyrolysis products [10,81,82].

The metallurgical industry is one of the key industries in developed countries [83]. Iron and steel production plays a key role in the global market economy. The world leader in iron and steel production is China, which supplies more than 50% of all raw materials in the metallurgical industry to the world market [84]. Metal products are the leading industrial material in almost every industry. Steel is of great importance for industry, urbanization and transport [34]. At the same time, the metallurgical industry is one of the most energy-intensive and polluting industries in the world [85]. These problems are met by the idea of a circular economy and the EU’s “Green Steel for Europe” program [86],

the aim of which is to decarbonize the steel industry [87], improve energy efficiency [88], achieve carbon neutrality and implement sustainability [89,90]. The transformation of the iron and steel industries is a long and complex process (Figure 11) [91]. Each mill has its own specificity of production, which involves individual adaptation of solutions to unique, already operating, process lines [92].

The metallurgical industry is currently intensifying its efforts to reduce CO₂ emissions [93]. At the same time, large-scale research is being carried out to reduce the use of fossil fuels or eliminate them altogether [94].

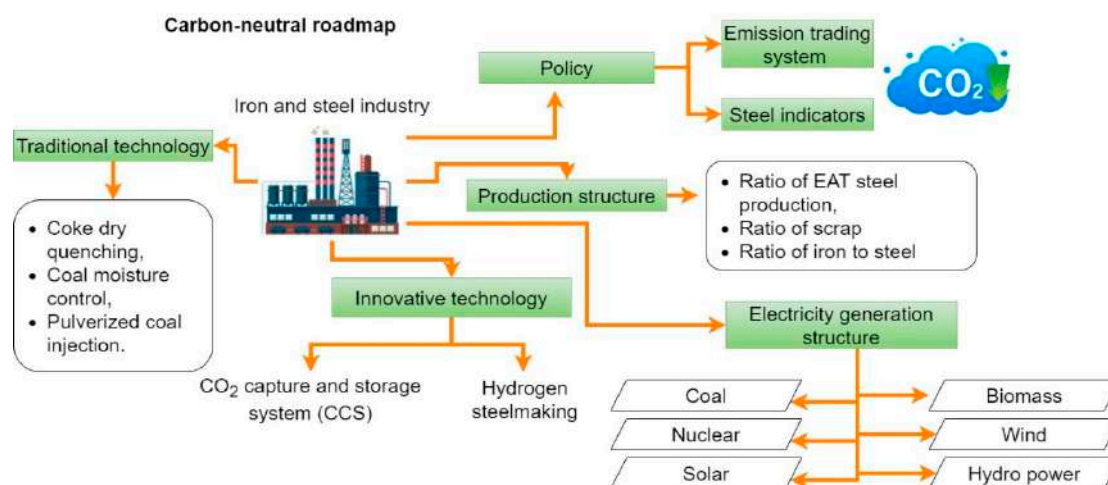


Figure 11. The path to decarbonization of the metallurgical industry [95].

The products of RDF pyrolysis show great potential for substituting conventional fuels. Countries such as Brazil show that it is possible to use biochar in the metallurgical industry. As much as 75% of total production of biochar in these countries goes to the iron and steel industries. In order for biochar to be used in metallurgy, it must meet strictly defined requirements, similar to those that characterize conventional fuels [96].

Biochar can replace conventional fuels in several stages of iron and steel production. Figure 12 shows the potential pathways for biochar to be introduced into the iron and steel production process [43]. Biochar can replace bituminous coal and coke in, among others:

- coke ovens;
- sintering processes;
- blast furnace processes;
- carbonization of liquid steel.

The metallurgical industry, as one of the most energy-intensive industries, consumes huge amounts of gaseous fuels. Just one of the mills operating in Poland consumes 2,500,000 Nm³ of natural gas per month. The monthly costs incurred by the company are EUR 5,575,000. In 2022, during the deepest energy crisis in recent years, the price of natural gas reached a staggering price of EUR 2.63 (the mean EUR: PLN exchange rate in 2022 was 1:4.68). Steelworks are trying to cut production costs by switching to coke oven gas supplied from coking plants. Unfortunately, the price of this gas has also increased almost 3 times (0.21 EUR). Taking into account the calorific value of gas from the pyrolysis of RDF, which varies from 20 to even 30 MJ/m³ [10,26,44,97], one can consider the use of pyrolysis gas for pre-heating furnaces before the plastic processing of metals [20]. Figure 13 compares the calorific values of conventional gaseous fuels with those of pyrolysis gas obtained from the pyrolysis of RDF.

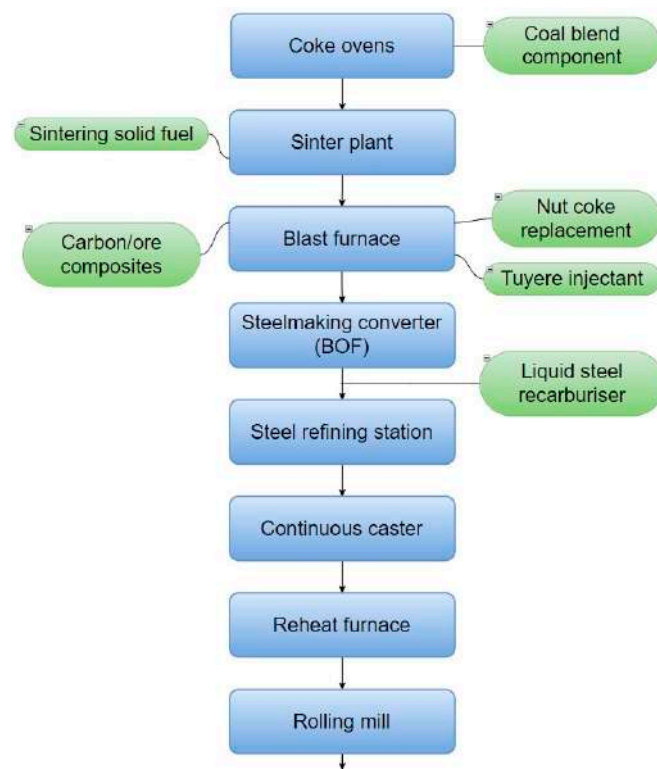


Figure 12. Biochar applications in metallurgy [95].

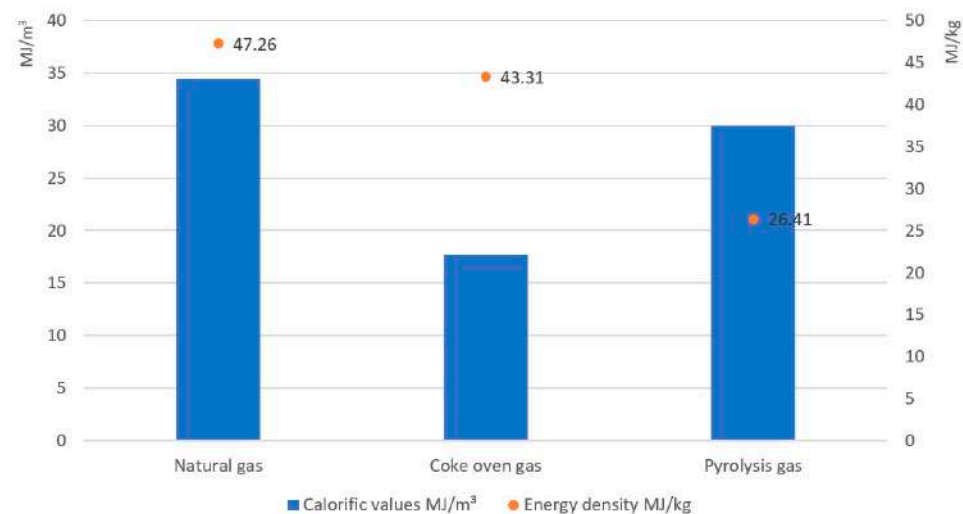


Figure 13. Comparison of the calorific values of conventional gaseous fuels with those of pyrolysis gas [9,10].

According to Szwaja et al. [67], it is possible to use gas obtained from thermal conversion (in this case from the torrefaction of biomass) for energy purposes in the metallurgical industry. The authors [20] proposed a concept of using torgas for firing pusher furnaces in the process of co-combustion with natural and coke-oven gases. The paper has shown that, despite low calorific value of torgas (6 MJ/Nm^3), its energy use offers economic benefits and, additionally, biochar is produced during the process, which can be used at other stages of iron and steel production. The use of gases from the thermal conversion of waste, for example pyrolysis, where the calorific value is much higher than in the case of torgas, may contribute to reducing the consumption of natural gas, which will ultimately allow the diversification of fuel and energy sources, while bringing measurable economic and environmental benefits [20,67].

4. Analysis of Strengths and Weaknesses of Generating Energy from RDF Pyrolysis Products

As suggested by numerous literature sources, the pyrolysis of RDF seems to be a promising solution [9,58]. The management of surplus RDF production has economic, environmental and social benefits. The use of RDF pyrolysis products for energy purposes, like any process, shows not only advantages but also disadvantages [47,98,99]. An analysis of these strengths and weaknesses is presented in Table 7.

Table 7. Strengths and weaknesses of using RDF pyrolysis products as energy sources [47,98,99].

Strengths	Weaknesses
(1) The generation of energy from the pyrolysis products offers environmental benefits: • More waste managed instead of landfilled; • Lower emissions of pollutants compared to conventional combustion; • Reduced production and use of conventional fossil fuels. (2) Pyrolysis is a very flexible process. By controlling the parameters of the process, you can get larger quantities of a more desirable product. (3) Pyrolysis is also suitable for the disposal of various types of waste, which is very beneficial considering diverse morphological compositions of RDF. (4) The pyrolysis plant does not require a large area, which enables integrating it into the existing infrastructure of the steelworks or other plant. (5) The conversion of RDF is in line with the ideas of circular economy. In addition, the products of RDF pyrolysis can be further used for generation of energy, which brings the metallurgical industry closer to carbon neutrality. (6) Continuous and intensive research on the pyrolysis process and the possibilities of managing its products enrich the world of science and bring the economy and industry closer to the introduction of pyrolysis for use on an industrial scale. (7) Finding new applications for pyrolysis products. Proposal to use pyrolysis gas and biochar for energy purposes, reducing the consumption of conventional fuels. (8) Possibility of co-financing investments from domestic sources (the National Fund for Environmental Protection and Water Management may co-finance up to 50% of eligible investment costs—up to PLN 50 million of non-returnable aid). Significant reduction of investment costs, which has a positive effect on the willingness to manage post-process products of the RDF pyrolysis. (9) The calorific values of pyrolysis gas and biochar are sufficient to treat them as attractive alternative fuels that can reduce process costs and bring the steel industry closer to carbon neutrality.	(1) RDF consists of a processed over-sieve fraction from the municipal waste stream. This involves additional processes (grinding, drying, pelletization) that the waste must undergo before it is delivered to the pyrolysis reactor. (2) The chlorine and sulfur contents in RDF, under certain process conditions, may corrode the plant, which may shorten the lifetime of the reactor, which will result in greater expenditures on maintenance. (3) Unknown investment costs: due to the lack of a pyrolysis plant operating on an industrial scale, investment and maintenance, and also profits, are just estimates at this stage, which discourages local governments and investors from building new pyrolysis systems. (4) Insufficient processing capacities of thermal waste disposal plans and lack of investment financing from the EU. (5) Lack of knowledge of the technology by the public, which may result in social reluctance at the stage of consultations or plans for the construction of infrastructure. Public opposition may effectively block or delay the finalization of the investment. (6) Low environmental awareness of the society, which may result in a lack of understanding of the need to obtain new sources of alternative fuels (a perception of no need to build new infrastructure for thermal conversion of waste). (7) Frequent incomprehensible changes in the law, too short time to implement changes, very high environmental standards to meet in a short time—all this gives rise to uncertainty that discourages companies from investing in new, prospective technologies.

5. Summary and Conclusions

The energy transformation taking place in Europe, additionally stimulated by the energy crisis resulting from the geopolitical situation and Russia's military operation against Ukraine, is a platform for the implementation of new solutions and technologies. One such solution is to replace fossil fuels with alternative ones. The use of RDF is in this case an example of a solution that allows for efficient use of industrial and municipal waste, thus reducing the amount of waste deposited in landfills and at the same time reducing the

demand for fossil fuels. This approach meets global trends in this area and is in line with the policy of sustainable development. RDF produced from the over-sieve fraction of waste can be used in many industries. The metallurgical industry looks particularly attractive in this case, as it seems to be the most absorbent industry for alternative fuels in the coming years. This is due to both technological conditions, production costs incurred by metallurgical companies, as well as the volume of production and the volume of demand for fuels. The use of biochar or, for example, gases from the thermal conversion of waste makes economic sense in this case [20]. Despite the investment and adaptation costs that the company must incur in the initial phase of technological transformation, in the long run it may bring measurable benefits to the steel industry, which will significantly compensate for the costs incurred. Already a 20% share of energy produced from biochar would give measurable effects in the form of a significant reduction in the relationship between the amount of carbon dioxide from non-renewable fossil fuels and the amount of carbon dioxide from alternative sources. These are arguments for the implementation of new technologies and the use of alternative fuels in the metallurgical industry. Reducing CO₂ emissions will have a positive impact on climate change by limiting the greenhouse effect, which will bring measurable benefits to the entire society [100].

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Review

Methods and Validation Techniques of Chemical Kinetics Models in Waste Thermal Conversion Processes

Magdalena Skrzyniarz ¹, Marcin Sajdak ², Anna Biniek-Poskart ³, Andrzej Skibiński ³, Marlena Krakowiak ¹, Andrzej Piotrowski ⁴, Patrycja Krasoń ¹ and Monika Zajemska ^{1,*}

¹ Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology, 19 Armii Krajowej Ave., 42-200 Czestochowa, Poland; magdalena.kocyba@pcz.pl (M.S.); marlena.krakowiak@pcz.pl (M.K.); patrycjakrason01@gmail.com (P.K.)

² Center of New Technologies, Department of Air Protection, Faculty of Energy and Environmental Engineering, Silesian University of Technology, 22 B Konarskiego Ave., 44-100 Gliwice, Poland; marcin.sajdak@polsl.pl

³ Faculty of Management, Czestochowa University of Technology, 19 B Armii Krajowej Ave., 42-200 Czestochowa, Poland; a.biniek-poskart@pcz.pl (A.B.-P.); andrzej.skibinski@pcz.pl (A.S.)

⁴ Faculty of Mechanical Engineering and Computer Science, Czestochowa University of Technology, 42-200 Czestochowa, Poland; andrzej.piotrowski@pcz.pl

* Correspondence: monika.zajemska@pcz.pl

Abstract: This article discusses the potential of using computer-simulation methods in processes such as thermal waste conversion, i.e., pyrolysis, gasification, combustion and torrefaction. These methods are gaining in importance, among others, due to the difficulties in execution and high costs associated with conducting experimental research in real conditions or the need to obtain detailed data on the phenomenon under study in a relatively short time. Computer simulation also allows for numerous errors to be avoided, such as those that may occur during optimization activities, the effects of which may have serious consequences, both economic and environmental. In addition to their many advantages, the limitations and disadvantages of using computer-simulation methods were also indicated, mainly related to the interpretation and validation of the results obtained using modelling. Owing to the complexity of the phenomena occurring during thermal conversion, special attention was focused on models based on chemical kinetics, thanks to which it is possible to predict the quantitative and qualitative composition of products in these processes. The aim of this research is to identify the research gap in the field of issues related to models of chemical kinetics of thermal waste conversion processes.

Keywords: simulation; circular economy; sustainable development; waste; thermal conversion; kinetic model



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1. Introduction

Efforts are being made worldwide to promote the energy use of waste through combustion [1], gasification [2], pyrolysis [3] and torrefaction [4] as a strategy that fits, among others, into the idea of a circular economy [5,6]. These activities focus on finding sustainable alternatives for the effective use of waste, which loses the status of “rubbish” and becomes a valuable raw material for other processes [1]. Unfortunately, due to the heterogeneity of waste and the complexity of the phenomena occurring during thermal conversion, there are a number of limitations to its widespread use [7].

The European Union strongly supports activities aimed at preventing waste and reusing products. According to the EU Landfill Directive, by 2035, EU countries must limit the amount of municipal waste sent to landfills to 10% or less of the total municipal waste generated [8]. This creates an opportunity to manage waste that has previously been stored in landfills. Currently, the EU places great emphasis on increasing the share of recycling in waste management methods and reducing the share of landfilling [9].

Examples include two neighboring countries: Poland and Germany. Both countries are striving to transition their economies to a circular economy. In this respect, Germany is considered to be a country that has made a number of far-reaching changes to achieve this goal. Currently, 79% of all waste generated in Germany (64% of municipal waste) is recycled (data from Statistische Bundesamt). In Poland, 36.3% of all waste generated (26.7% of municipal waste) was recycled in 2022—according to data from the Central Statistical Office (called GUS in Poland). Both countries mentioned above have a similar hierarchy of waste management (Figure 1).



Figure 1. Hierarchy of treatment of non-hazardous waste [9,10].

Germany has introduced the “Principles for Sustainable Waste Management”, which contributes to the elimination of waste. These rules specify that the producer is responsible for each waste produced (also financially—“the polluter pays”). This encourages manufacturers to create new products responsibly. The “precautionary principle” allows for intervention in areas where general regulations do not function adequately. The “principle of proximity” requires that waste be disposed of as close as possible to the place of its generation, which does not exclude the export of waste if it is economically profitable. The “principle of subsidiarity” determines who will deal with waste management, taking into account factors such as transport costs, efficiency and benefits resulting from the proximity of the place of waste production and processing [11]. A special group of waste is chemical waste that, due to its properties (flammability, explosiveness, toxicity and others), is classified as hazardous waste [12–14] and requires proper handling [15], with particular care. Chemical waste includes waste oils [16], waste-containing asbestos, medical and veterinary waste, expired plant protection products and household chemicals [17]. As numerous scientific works indicate, hazardous waste is the most difficult waste to manage because, in the process of its thermal processing, it produces, among others, heavy metals and dioxins. Governments around the world are making a number of efforts to better manage and deal with hazardous waste. An example is Portugal. Over the last decades, the Portuguese government has introduced numerous solutions, such as the modification of the legal framework, creation of a network infrastructure that includes integrated systems of industrial waste treatment (ISIWT) and also development of new organizational methods to make the waste management system more effective [16].

Widely developed computerization addresses these problems by proposing numerical-simulation methods as an important tool in the analysis of complex chemical and gasodynamic phenomena occurring during the thermal conversion of waste [18,19]. The interest in using computer-simulation methods in thermal waste conversion processes is evidenced

by numerous scientific publications [20,21]. Using the popular science mapping tool VOSviewer (version 1.6.20) [20–23], an analysis was carried out using the Scopus database.

The datasets prepared on the basis of the Scopus database include an analysis of global literature on research topics focusing on chemical kinetics in relation to thermal conversion of waste. The research was performed in May 2024. The results of the literature analysis are based on the use of keywords and restrictions introduced in the advanced search in the Scopus database. In order to limit the number of documents found, only the titles of articles were analyzed (not abstracts and keywords). The search with the use of the string “TITLE-ABS-KEY” resulted in finding over a thousand documents that were not necessarily connected with the analyzed subject matter. The used string was as follows: TITLE (“chemical kinetics” OR “chemical models” OR “kinetics model” OR “kinetic theory” OR “kinetics” OR “kinetic modeling”) AND (“waste”) AND (“thermal conversion” OR “gasification” OR “combustion” OR “torrefaction” OR “pyrolysis”) AND PUBYEAR > 2018 AND PUBYEAR < 2026 AND (LIMIT-TO (SRCTYPE, “j”)). The number of results found was 212 documents. The timeframe was limited to the last six years, and the searching formula was limited only to article titles that appear in journals. Then, the results selected from the Scopus database were exported as CSV files and supplied into the VOSviewer program in order to analyze the correlations of the obtained literature list for a given subject area. The observed dependencies and relationships between the selected keywords required the creation of several datasets. Visualizations in the form of a map were created using the VOSviewer 1.6.18 software. As part of the attempt to interpret the keywords, the following approach was taken: the type of analysis was “co-occurrence”, the unit of analysis was “All keywords”, and the counting method was “Full counting”. The “minimum number of occurrences of a keyword” was set to six. This led to 142 results as those that “meet the threshold” among 2005 keywords. If the minimal number of occurrences of a keyword was five, the results that meet the threshold were 175. If that number was seven, it led to 107 results, and if the number was eight, the number of results was 89. Two of all the keywords were eliminated due to the lack of their importance to the subject matter, and they were “article” and “priority journal”. Figure 2 as well as Figure 3 show that the most frequently appearing words were kinetics, activation energy and pyrolysis with the total link strength of 1571, 1570 and 1561, respectively. However, the ranking of a keyword’s total link strength may differ a bit from that of their occurrences.

Selected	Keyword	Occurrences	Total link strength
☒	kinetics	141	1571
☒	activation energy	137	1570
☒	pyrolysis	144	1561
☒	thermogravimetric analysis	81	943
☒	reaction kinetics	63	793
☒	biomass	52	614
☒	thermogravimetry	36	597
☐	article	33	583
☒	kinetic parameters	37	487
☒	pyrolysis kinetics	45	451
☒	heating	26	398
☒	copyrolysis	26	354
☒	waste incineration	29	332
☒	fourier transform infrared spectroscopy	21	311
☒	temperature	20	308
☒	thermodynamics	21	298
☒	co-pyrolysis	28	293
☒	decomposition	16	281
☒	controlled study	14	277
☒	priority journal	14	276

Figure 2. Screenshot of top 20 keywords indicated by the VOSviewer with their number of occurrences and total link strength.

Among a total number of 2005 keywords, there were three that appear with a frequency of over 130 times; one keyword with a frequency of over 80, 60, 50 and 40 times each; and seven keywords with a frequency of over 20 times.

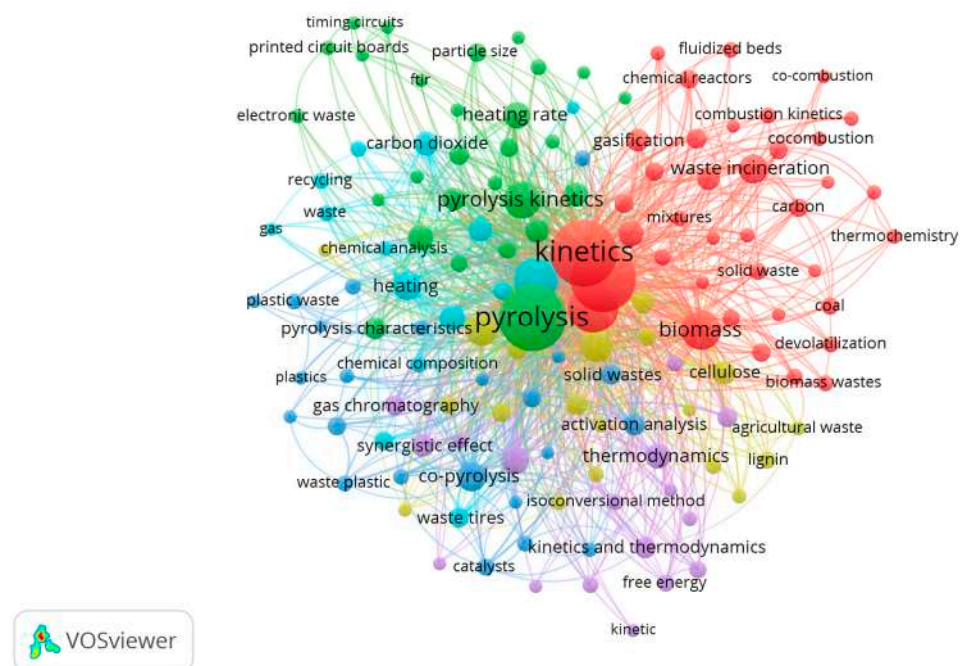


Figure 3. VOSviewer network visualization of keyword co-occurrence.

Using the VOSviewer software, the correlation between particular keywords that appear in documents being analyzed can be identified and presented as a map. The words are grouped into clusters to show their relationship. The size of the circles is positively correlated with the occurrence of the keywords. The more often a keyword appears, the larger the font size and circles. The strength of occurrences is indicated by the size of the nodes, while the strength of the relationships reflects the thickness of the lines between the nodes. The analysis shows that five clusters were identified in the network (red, green, blue, purple and yellow). The red cluster is connected with the keyword “kinetics” that indicates 139 links, “activation energy” with 139 links, “thermogravimetric analysis” with 136 links, as well as “biomass” indicating 121 links and “waste incineration” with 102 links. The green cluster refers to the keyword “pyrolysis”, indicating 137 links, correlated with “pyrolysis kinetics”. The connectivity included in the blue, purple and yellow clusters is less dominant, which is presented by the size of their circles.

Analyzing the “network” visualization, it was observed that, over the years, interest in chemical kinetics in the thermal conversion of waste processes has been growing. This is confirmed by the network of connections within the clusters. The keyword maps clearly indicate the high importance of the research topic undertaken, emphasizing the need to expand research in this area, especially in the context of predicting the chemical composition of thermal waste conversion products using chemical kinetics models. The analysis shows that, despite many scientific works published on this topic, there is still a research gap in the issues discussed in the article. With a view to promoting a sustainable development strategy around the world in which the effective use of waste (with diverse properties and elemental composition) plays an important role, there is an urgent need to develop mathematical models that take into account the chemical kinetics of thermal waste conversion. The use of computer-simulation methods in the analysis of complex thermal decomposition processes will assess their energy suitability and the environmental effects of their use.

2. Theoretical Background

2.1. The Essence of Computer Simulations

As a result of the development of technology, computer-simulation methods have been gaining importance in recent years, being used not only in many industries but also in business and government institutions [24]. Simulation takes various forms from

modelling simple systems and systems for operational management purposes, such as production and finance, to modelling complex systems for corporations, the global economy or environmental organizations [25,26]. In the initial stages of the development of simulation methods, simulations were used primarily in the natural, technical and economic sciences [23,26,27]. They are currently widely used on a wide scale in various industries, such as the automotive industry [25,28] (Nissan, PSA Peugeot Citroën, Toyota, Ford Motor Company) and fields of science, in particular global scientific and research centers [29] (the Universities of Michigan, Tokyo, Minnesota, Karlsruhe and Colorado) as well as by the National Aeronautics and Space Administration (NASA) [30–32]. Currently, there is even a trend of the overuse of computer-simulation methods, which can be explained not only by the degree of development of science but also by the ease and universality of their usage. The appropriate use of computer-simulation methods may be determined by many factors, in particular [23,33] the following:

- Too high costs of conducting experimental research in real conditions;
- The need to quickly obtain accurate data on the phenomenon under study;
- The need to obtain a range of information that is impossible to obtain exponentially, which will complement and enrich the existing state of knowledge;
- The need to avoid mistakes whose consequences may be serious;
- The lack of an actual research object or when it is only at the design stage.

Numerical models typically consist of input data, decision variables and output data (Figure 4) [34–37]. Input data introduce constant values into the model for a single experiment, while decision variables are variables controlled by the researcher. The output data are determined by the input and decision data; they enable the selection of a certain combination of decision variable values that is best from the point of view of the analyzed problem.

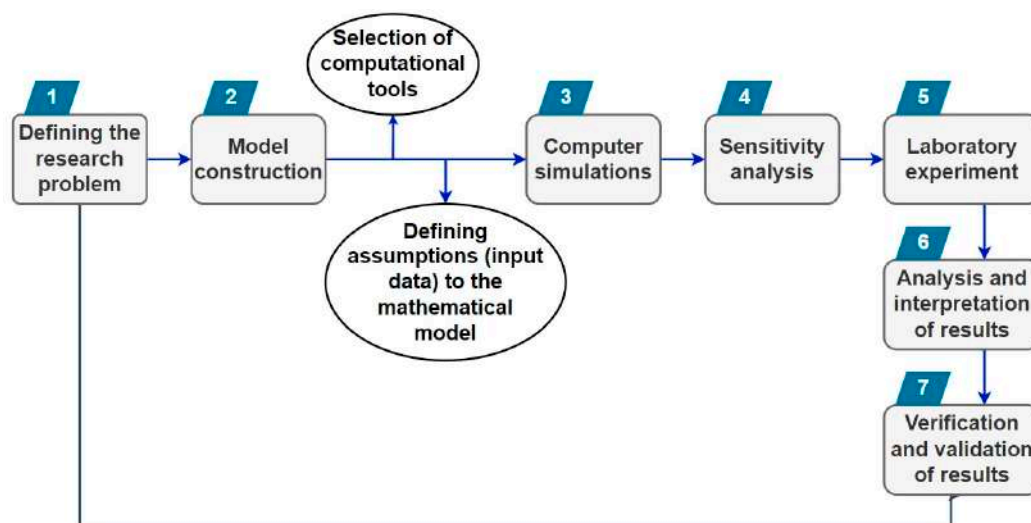


Figure 4. Stages of computer simulation [33].

The greatest advantage of computer simulations is the ability to analyze various time periods with a full picture of the phenomena occurring at each stage of the analyzed process. This is extremely difficult or even impossible to observe in real conditions. A great advantage of simulation is also the repeatability of processes because, once the model has been developed, it can simulate the process any number of times. In addition, the model can incorporate various variants, such as forcing, interference and other changes. The cost of building a model is, in many cases, much lower than conducting research in real conditions, and the possibilities of interpreting the results increase with the number of recorded parameters. However, it is important to note that both the design and interpretation of simulation results require experience and skills to include all relevant parameters and

variables for a given process in the simulated problem. Therefore, the main disadvantage of computer simulations is the possibility of making an error when creating the model and the difficulty in properly interpreting the simulation results. These issues are caused by the human factor since a person creates the simulation model and may incorrectly formulate the simulated problem and adjust the tool as well as draw incorrect conclusions from the simulations (Figure 5) [38–40].

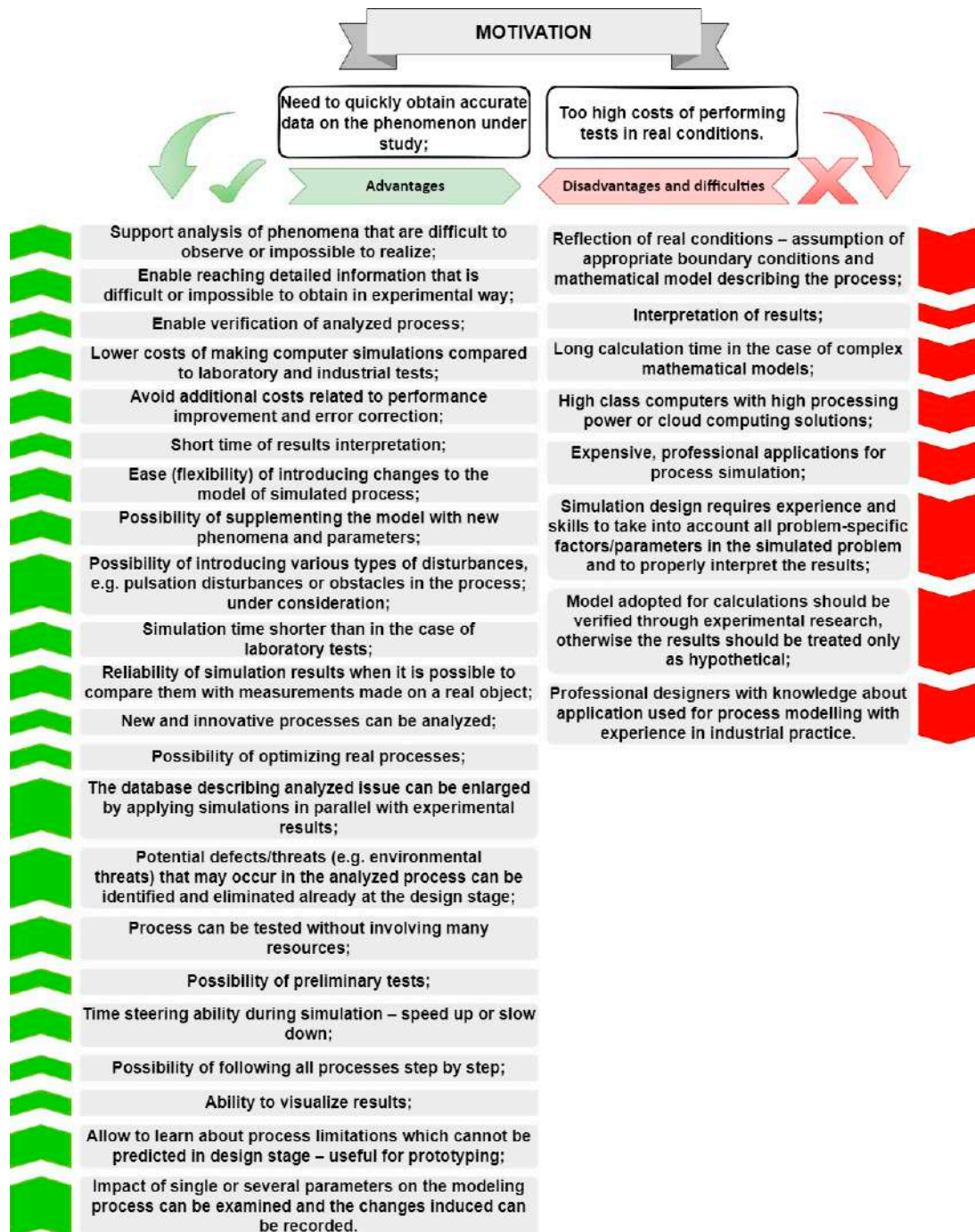


Figure 5. Motivation, advantages and disadvantages of computer simulations [21,33,39,40].

2.2. Application of Numerical-Simulation Methods in the Analysis of Thermal Conversion Processes of Fuels and Waste

As numerous scientific works indicate, the main way to produce cleaner energy [41,42], especially in the era of energy transformation and decarbonization [43], is to employ thermal

conversion processes such as pyrolysis [44–46], combustion [47–49], gasification [50–54] or torrefaction [55,56]. The input material in the above-mentioned processes includes not only commonly used biomass [18,57,58] but also various types of waste [59,60], including plastics (e.g., PP, PET, PE) [61–64], municipal solid waste (MSW) [65], waste from the recycling of scrap tires [66,67], rural domestic waste [68] and refuse-derived fuel (RDF) [69–72] and solid recovered fuel (SRF) [73]. The initial stage of both combustion and gasification is pyrolysis [74,75].

Numerous scientific and research centers are attempting to increase the share of waste in energy production through thermal conversion [76,77]. However, providing a comprehensive description of thermal degradation is highly problematic due to the complexity of these processes [18,78,79]. The urgent need to understand and optimize these processes [80] has contributed in recent years to intensive development in the elaboration of numerical models [81,82], and the main research efforts are focused on understanding the reaction mechanisms of the kinetics of thermal conversion processes [83–85]. Chemical kinetics is crucial in comprehending the complex chemistry of the reactions of these processes and the creation of mathematical models [86–89].

Thermal conversion processes can be simulated using three different approaches:

- i. Computational fluid dynamics models [47,90–93];
- ii. Kinetic models [18,94,95];
- iii. Equilibrium models [52,96–98].

Equilibrium models are generally easy to implement, among others, due to numerous simplifications [99] (Figure 6). Depending on the method used to calculate chemical equilibrium, equilibrium models can be classified into two categories:

- i. Stoichiometric models;
- ii. Non-stoichiometric models.

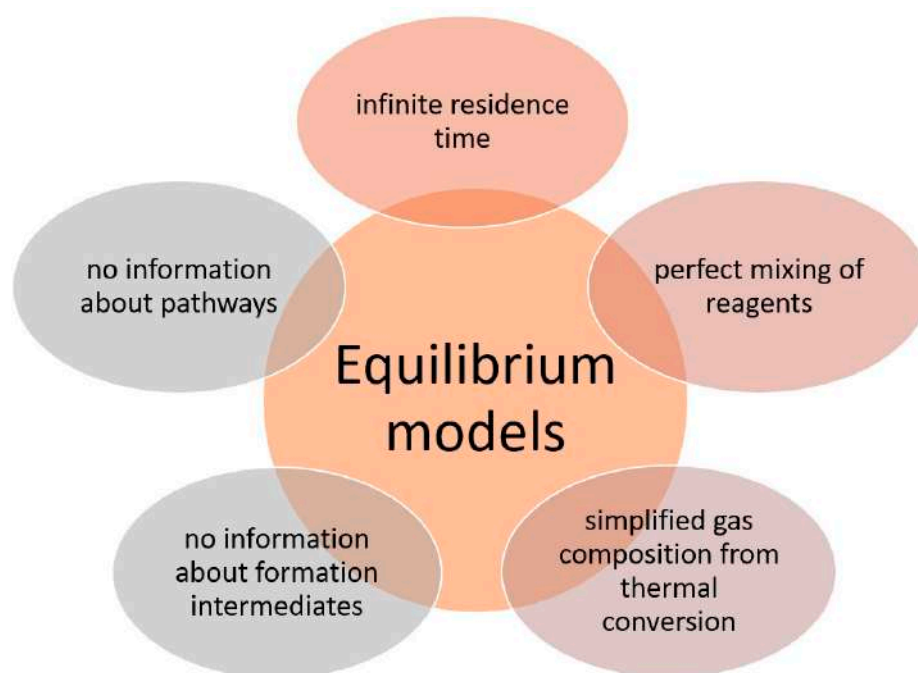


Figure 6. Simplifications of equilibrium models [99].

In stoichiometric models, the equilibrium is determined by using equilibrium constants for each reaction involved in the analyzed process. In contrast, in non-stoichiometric models, it is determined by minimizing the Gibbs free energy [38].

Kinetic modelling is quite complex [100], and the models are divided into the following:

- Lumped models [75,101,102];
- Other distributed kinetic models [103–107].

Most of the models described in the literature are simplified models that only allow for the prediction of the char yield and degassing time [108,109]. Unfortunately, this approach is not sufficient. From the energetic point of view of thermal conversion processes, it is extremely important to provide information on the temperature distribution, kinetic parameters and chemical composition of the gases released during the above-mentioned processes [98,110]. Although these issues have been extensively studied both theoretically and experimentally using various techniques, they still require more attention and research [111–113]. Thermal analysis techniques, such as (TG) [107], (DSC), (DTA), FTIR [114], MS or various combinations thereof, i.e., (TG–FTIR) [115], (TG–MS) or (TG–MS–FTIR), are considered effective techniques for examining the thermal degradation of both fuels and waste. The above-mentioned techniques provide information about the analyzed processes, enabling a better understanding of them, and above all, they can constitute input data for computer simulations [116–118].

Table 1 lists the thermal conversion processes in which computer simulations were employed.

Table 1. Use of computer simulations to predict products of thermal conversion of biomass.

Process	Feedstock Type	Kinetic Mechanism	Res.
Pyrolysis Single-step and multi-step thermos kinetic study multi-step mechanism reaction	Biomass: grass <i>Eleusine indica</i>	Eleusine indica $\left\{ \begin{array}{l} \text{Hemicellulose} \xrightarrow{k_h} \text{Volatiles} + \text{Char} \\ \text{Cellulose} \xrightarrow{k_c} \text{Volatiles} + \text{Char} \\ \text{Lignin} \xrightarrow{k_l} \text{Volatiles} + \text{Char} \end{array} \right.$	[119]
	Kinetic triplets	Catole coconut $\left\{ \begin{array}{l} \text{Hemicellulose} \xrightarrow{k_h} \text{Volatiles} + \text{Char} \\ \text{Cellulose} \xrightarrow{k_c} \text{Volatiles} + \text{Char} \\ \text{Lignin} \xrightarrow{k_l} \text{Volatiles} + \text{Char} \end{array} \right.$	[120]
	Butia seed waste (BSW)	BSW $\left\{ \begin{array}{l} \text{Extractives} \xrightarrow{k_e} \text{Volatiles} + \text{Char} \\ \text{Hemicellulose} \xrightarrow{k_h} \text{Volatiles} + \text{Char} \\ \text{Cellulose} \xrightarrow{k_c} \text{Volatiles} + \text{Char} \\ \text{Lignin} \xrightarrow{k_l} \text{Volatiles} + \text{Char} \end{array} \right.$	[121]
	Pecan nutshell	PNS $\left\{ \begin{array}{l} \text{Hemicellulose} \xrightarrow{k_h} \text{Volatiles} + \text{Char} \\ \text{Cellulose} \xrightarrow{k_c} \text{Volatiles} + \text{Char} \\ \text{Lignin} \xrightarrow{k_l} \text{Volatiles} + \text{Char} \end{array} \right.$	[122]
	Macauba endocarp (<i>Acrocomia aculeate</i>)	Macauba endocarp $\left\{ \begin{array}{l} \text{Hemicellulose} \xrightarrow{k_h} \text{Volatiles} + \text{Char} \\ \text{Cellulose} \xrightarrow{k_c} \text{Volatiles} + \text{Char} \\ \text{Lignin} \xrightarrow{k_l} \text{Volatiles} + \text{Char} \end{array} \right.$	[123]
Pyrolysis	Royal palm tree waste	(Royal palm tree waste) $\left\{ \begin{array}{l} \text{Extractives} \xrightarrow{k_e} \text{Volatiles} + \text{Char} \\ \text{Hemicellulose} \xrightarrow{k_h} \text{Volatiles} + \text{Char} \\ \text{Cellulose} \xrightarrow{k_c} \text{Volatiles} + \text{Char} \\ \text{Lignin} \xrightarrow{k_l} \text{Volatiles} + \text{Char} \end{array} \right.$	[124]
Pyrolysis	Poplar and eucalyptus wood sawdust	The kinetic parameters were computed via model-fitting (inflection point and multiple linear regression) and model-free (OFW and KAS) methods.	[125]
Thermal conversion	<i>Bambusa vulgaris</i> dust (BD) and delonix regia pods peels (DRP)	Model-free methods, like Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO), were applied for the determination of kinetic parameters.	[126]
Pyrolysis	<i>Sesbania bispinosa</i>	The three-pseudo-component model is made up of hemicellulose, cellulose and lignin. Artificial neural networks (ANN) are models based on the operation of the human brain.	[104]

Table 1. Cont.

Process	Feedstock Type	Kinetic Mechanism	Res.
Combustion	Biomass	Cellulose, hemicellulose, lignin, biomass $\xrightarrow{1}$ Active intermediate $\xrightarrow{2}$ Volatiles $\xrightarrow{4}$ Gas $\xrightarrow{3}$ Y Char + (1 - Y)Gas (1) Biomass $\rightarrow$ Tars (2) Biomass $\rightarrow$ Volatiles (3) Biomass $\rightarrow$ Char (4) Tars $\rightarrow$ Volatiles (5) Tars $\rightarrow$ Char (6) Char + O ₂ $\rightarrow$ CO ₂ (7) Char + CO ₂ $\rightarrow$ 2 CO (8) Char + H ₂ O $\rightarrow$ CO + H ₂	[48]
Pyrolysis		Mango seed waste $\left\{ \begin{array}{l} \text{Extractives} \xrightarrow{k_e} \text{Volatiles} + \text{Char} \\ \text{Hemicellulose} \xrightarrow{k_h} \text{Volatiles} + \text{Char} \\ \text{Cellulose} \xrightarrow{k_c} \text{Volatiles} + \text{Char} \\ \text{Lignin} \xrightarrow{k_l} \text{Volatiles} + \text{Char} \end{array} \right.$	[127]
Pyrolysis	Virgin	Cellulose, hemicellulose, lignin (Virgin biomass) $\xrightarrow{k_1}$ Active biomasse $\left\{ \begin{array}{l} \xrightarrow{k_3} (1-Y)\text{Gas} + Y\text{Biochar} \\ \xrightarrow{k_2} \text{Tar} \end{array} \right.$ $\xrightarrow{k_4}$ Tar	[128]
Pyrolysis three-independent parallel reactions model	Beech wood, Rice husk	A three-independent-parallel-reactions model is used to model the kinetics of total devolatilization.	[75]
The two-step kinetic model proposed by Koufopoulos et al. for lignocellulosic biomass pyrolysis	Wood sawdust, bagasse, peanut hull, douglas fir bark, and rice husk		[129]
Torrefaction process	Beechwood	- lump kinetic scheme; - detailed kinetic scheme developed by Andr�es and Ingwald; - detailed kinetic scheme developed by Debiagi et al. with a one-dimensional model.	[130]
Pyrolysis		Wood $\left\{ \begin{array}{l} \xrightarrow{k_C} \text{Char} \\ \xrightarrow{k_L} \text{Tars} \\ \xrightarrow{k_G} \text{Gas} \end{array} \right.$ $k = k_C + k_L + k_G$ One-component mechanism of primary wood pyrolysis proposed by Shafizadeh and Chin. Multi-component (or multi-stage) mechanisms of wood/biomass pyrolysis.	[131]
Pyrolysis	Biomass	(A) Cellulose $\xrightarrow{k}$ tar + coal + gasext (B) Hemicellulose $\xrightarrow{k_{11}}$ 0.063 volatile matter I + 0.820 solid intermediate I $\xrightarrow{k_2}$ 0.310 volatile matter + 0.690 solid intermediate II $\xrightarrow{k_{31}}$ 0.900 volatile matter $\xrightarrow{k_{12}}$ 0.117 volatile matter II $\xrightarrow{k_{32}}$ 0.300 gases + 0.610 coal (C) Lignin $\xrightarrow{k_{11}}$ 0.300 volatile matter I + 0.600 solid intermediate $\xrightarrow{k_{21}}$ 0.090 volatile matter $\xrightarrow{k_{12}}$ 0.100 volatile matter II $\xrightarrow{k_{22}}$ 0.300 gases + 0.610 coal Comprehensive kinetic models for pyrolysis of cellulose, hemicellulose and lignin.	[126]
Combustion	Polyethylene	A Non-isothermal 1D model	[132]
Gasification process	Pine sawdust	Comprehensive model was developed by Aspen Plus.	[133]
Pyrolysis	Wood, grass, and crops	Chemical reaction neural networks (CRNN) model	[58]

Table 1. Cont.

Process	Feedstock Type	Kinetic Mechanism	Res.
Pyrolysis	Biomass	Two-stage semi-global mechanism (CFD) <i>Primary reaction</i> <i>Secondary reaction</i>	[134]
Gasification		Main kinetic schemes for wood gasification: (1) Wood $\rightarrow \begin{cases} \text{Gas} \\ \text{Tar} \\ \text{Char} \end{cases} \rightarrow \text{Tar} \rightarrow \begin{cases} \text{Gas} \\ \text{Char} \end{cases}$ (2) Cellulose $\rightarrow$ Cellulose Active $\rightarrow \begin{cases} \text{Tar} \\ \text{Char} + \text{Gas} \end{cases} \rightarrow \text{Tar} \rightarrow \text{Gas}$ (3) Virgin Biomass $\rightarrow \begin{cases} \text{Volite} + \text{Gases} \\ \text{Char} \end{cases} \rightarrow \begin{cases} \text{Volite} + \text{Gases} \\ \text{Char} \end{cases}$	[51]
Pyrolysis	Polietylen, polipropylen, politereftalan etylenu		[116]
Pyrolysis	Empty fruit bunch	A simplified first-order gasification reaction model	[135]
			[136]
Torrefaction	Willow		[86]

According to the analysis, researchers have most often used the equation describing the relationship to explain the phenomena occurring during the thermal conversion of biomass and, in particular, pyrolysis (1) [104]:

$$\text{Biomass (SB)} \xrightarrow{K(t)} \text{Volatile(condensable + non condensable)} + \text{Biochar} \quad (1)$$

Che et al. [137] noted that Huazhong University of Science and Technology State Key Laboratory of Coal Combustion made significant advancements in the numerical simulation of gasification technology. Yang Haiping utilized the HSC chemistry package and the PSR reactor model to simulate the thermodynamic equilibrium and dynamic equilibrium of the palm oil waste pyrolysis process. The results obtained by Haiping revealed that the initial products contain significant amounts of H_2 , CO , CO_2 , CH_4 , H_2O and coke and small amounts of C_2H_2 , C_2H_6 , C_3H_8 and others in addition to the concentrations of H_2 and CO , which grow with the rise in the pyrolysis temperature.

Noteworthy are the computer simulations conducted by Peters et al. [138], who modelled the biomass pyrolysis process using an innovative reaction model in the Aspen Plus (version v14) program. This model was based on the three main building blocks of woody biomass, namely cellulose, hemicellulose and lignin. The pyrolysis process was described using 149 reactions. The linear regression algorithm took into account secondary pyrolysis reactions, enabling the calculation of slow and intermediate pyrolysis reactions. The model of bio-oil included chemical compounds, such as organic acids, aldehydes, alcohols, ketones, phenols, sugar derivatives and degraded lignin, and the produced carbon was modelled implementing the actual elemental composition.

A diagram of the reaction mechanism employed by Petersen et al. is presented in Figure 7 [138].

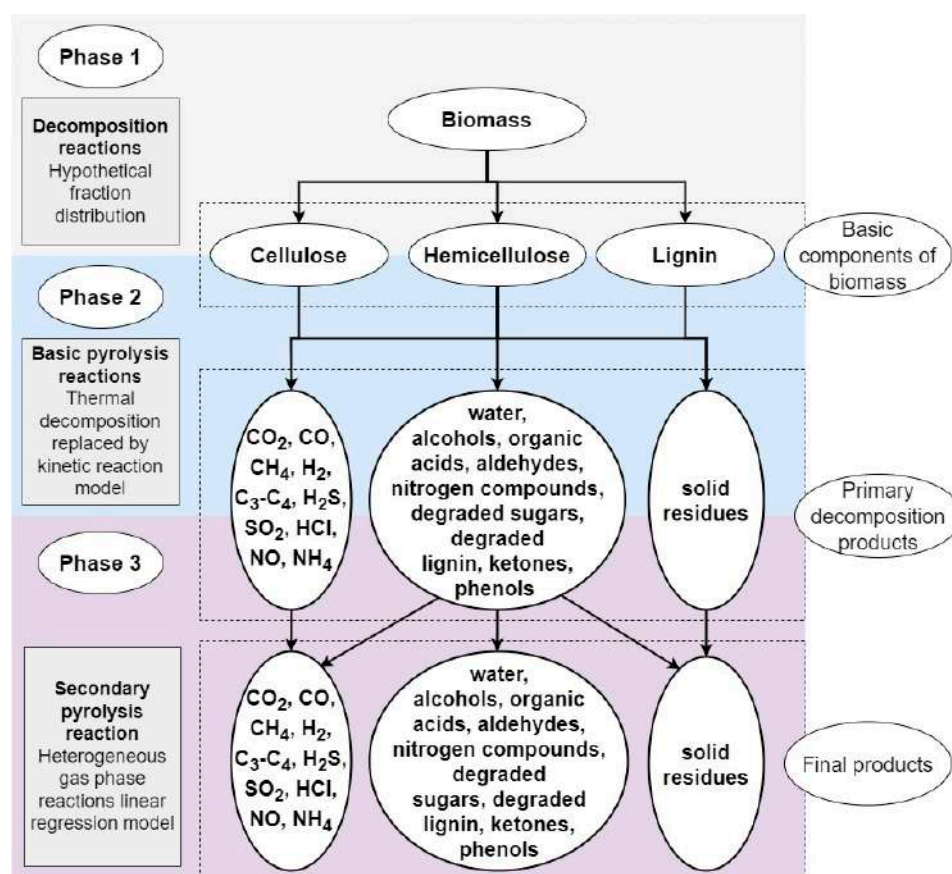


Figure 7. Three-stage pyrolysis reaction diagram [138].

The above model takes into account primary pyrolysis reactions as well as secondary cracking reactions. The pyrolysis mechanism was divided into three phases, namely one decomposition phase and two pyrolysis phases. The first phase is a virtual reaction step that breaks down the biomass into three main biochemical building blocks: cellulose, hemicellulose and lignin. During the second phase, the decomposition and volatilization of biomass fragments took place, leading to high efficiency of the liquid fraction. This is the dominant reaction mechanism for fast pyrolysis processes with short gas residence times. The third phase involved secondary cracking and charring reactions, which increased the gas and carbon yields at the expense of liquid yields as a consequence of secondary (catalytic) cracking reactions. These reactions are more significant with the increasing residence time and are, therefore, particularly important for slow and intermediate pyrolysis reactions. Petersen et al. [138] proposed a model that allows for the simulation of fast and slow pyrolysis of any lignocellulosic raw material with a known composition [138]. Moreover, a predictive and detailed modelling approach enabled a comprehensive assessment of

the properties of bio-oils obtained from various types of lignocellulosic biomass under various pyrolysis conditions (including fast and slow pyrolysis). Peters et al. emphasize that, to date, the analysis of pyrolysis processes has been based on simple models with a very simplified composition of bio-oil. The authors point out that their work is the first to present a comprehensive kinetic model of the reaction, which can be easily implemented in Aspen Plus and similar thermal conversion simulation software packages.

A similar approach was proposed by Granados et al., who modelled the biomass torrefaction process consisting of the three stages previously described in Petersen's work [139]. The process starts with drying the biomass to remove moisture, followed by heating the completely dry biomass. When the temperature grows, the biomass degassing process begins, resulting in the formation of condensable and non-condensable volatile substances and a solid residue. At low temperatures, the hemicellulose decomposition rate is high and dominates the entire torrefaction process. Only at high temperatures do some of the cellulose and lignin also begin to decompose but to a lesser extent. After primary degassing, secondary reactions occur where the produced condensable volatiles can react and form new solid and volatile components [139].

Park et al. [140] proposed a simplified approach to modelling the thermal conversion of biomass. Using Aspen Plus (version 14.3) software, they modelled the impact of the process operating conditions on biomass torrefaction using a one-dimensional reactor. The input data for the modelling were taken from the literature, and the diagram of the kinetic mechanism is presented in Figure 8. The results obtained by Park et al. confirmed that the energy efficiency of the torrefaction process increases with temperature (Figure 8).

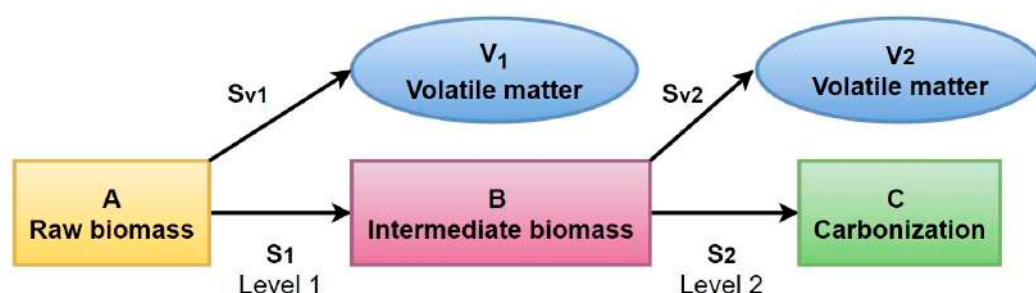


Figure 8. The scheme of chemical reaction kinetics mechanism proposed by Park et al. [140].

Yet another approach was proposed by Bates et al. [141], who developed a kinetic model for estimating the torrefaction products. The model is based on the mechanism originally proposed by Di Blasi and Lanzetta for the degradation of pure hemicellulose. Oliviera et al. [142] developed a kinetic model of the solid waste gasification process. The proposed mathematical model allowed for the detailed analysis of the processes occurring during gasification, taking into account partial derivatives, through the use of a CFD tool.

Also noteworthy is the approach to modelling the thermal conversion of biomass proposed by Wang et al. [126]. The authors developed a model for predicting pyrolysis products based on the Coats–Redfern method and the Kissinger method (Figure 9).

Yet another approach to simulating the biomass gasification process was proposed in the work by Gambarotta [42], who used a non-stoichiometric equilibrium model in downdraft gasifiers. The author utilized a five-component composition of the raw material for the calculations, i.e., forest waste (carbon, hydrogen, oxygen, nitrogen and sulfur), and included fifteen chemical compounds for the synthesis gas. The model calculated the relative amounts of gasification products and the calorific value of the synthesis gas. Gambarotta emphasized that the advantage of the non-stoichiometric approach is that it can easily calculate not only the concentrations of the main gasification products but also the concentrations of the by-products, especially chemical compounds containing nitrogen and sulfur. At the same time, he pointed out one of the main disadvantages of equilibrium models, namely the overestimation of molecular hydrogen and the underestimation of methane. The model developed by Gambarotta was analyzed for the sensitivity of the

influence of the selected parameters on the process and then verified by comparing the obtained simulation results with experimental data found in the literature. The model occurred to be effective in simulating the biomass gasification process with an acceptable level of error.

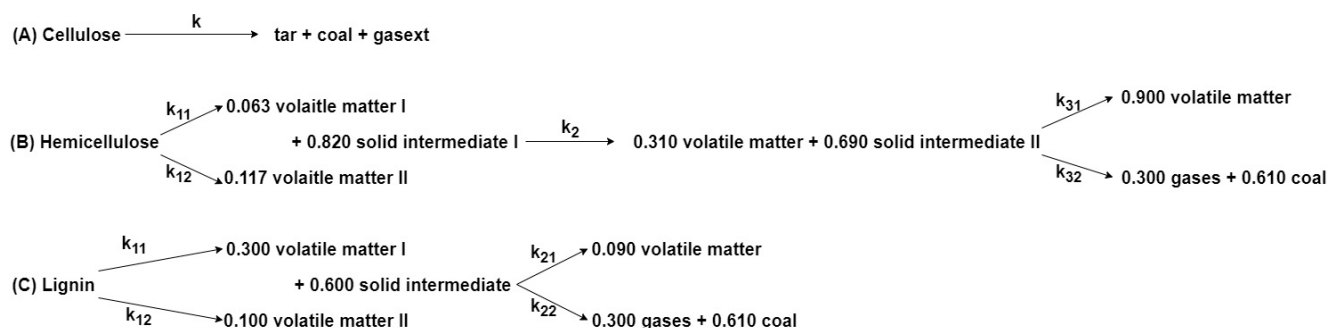


Figure 9. Model according to Wang et al. [126].

The actual reaction patterns of waste pyrolysis, including biomass and plastics, are extremely complex due to the formation of over one hundred intermediate products [117,143,144]. RDF is a special type of waste that is more complex than biomass due to its heterogeneous nature [72]. The amount of research on the kinetic modelling of RDF is much smaller compared to other fuels [71,145,146]. Three different approaches have been used in the literature to model the kinetics of thermal degradation of complex solid fuels, such as RDF. The first one considers fuel as one homogeneous species. The second approach considers the RDF pyrolysis rate as a weighted sum of the pyrolysis rates of cellulose, lignin, hemicellulose, polyethylene and other plastics. The third approach, similar to the second, considers the RDF pyrolysis rate as the weighted sum of the pyrolysis rates of paper, cardboard, wood, polyethylene and other plastics. The second and third approaches assume that possible interactions between the RDF components have a negligible impact on pyrolysis [71,146].

The research conducted by Zhou et al. [144] deserves attention. The authors developed a model to describe the heat transfer processes inside a porous RDF particle composed of polyethylene and cardboard. The model also considers the heat of the fusion of polyethylene (PE). To describe the degradation of polyethylene and cardboard, the authors adopted a one-stage global model and a scheme of two consecutive first-order reactions. To match the results of experimental research, the authors selected and modified two widely used heat transfer models—the Kunii and Smith model and the Breitbach and Barthels model. Moreover, they investigated the influence of the heat transfer model on the prediction of the RDF pyrolysis process. The authors achieved a high level of agreement between the results obtained through modelling and the experimental results for both the modified Kunia and Smith model and for the Breitbach and Barthels model.

On the other hand, Çepelioğullar et al. [146] modelled the pyrolysis process of RDF fuel in four reaction stages. The authors observed that the thermal decomposition of RDF involved many stages, which consisted of the decomposition of cellulose and plastics. Similarly, Bosmans et al. [147], using MATLAB (version R2023a) software, modelled the RDF fuel pyrolysis process, assuming four independent, parallel first-order reactions. The model adopted for the calculations enabled high compliance and a good fit with the experimental data since it was able to capture both the degradation of the lignocellulosic fraction and the plastic fraction in the waste material. The authors recommend that researchers conduct TGA experiments on RDF samples to obtain a full picture of the material degradation process. If RDF was produced from household waste, the DTG degradation profile of this waste may match those reported in the literature. Nonetheless, if RDF was created from different waste streams and was heterogeneous, it is unlikely that a similar DTG profile would be found in the literature. By combining the obtained pyrolysis kinetics with heat and mass transfer, accurate simulation models for real thermochemical conversion systems can be obtained [147].

2.3. Tools for Numerical Simulation of Thermal Conversion Processes of Fuels and Waste

Among the most frequently mentioned programs for simulating thermal conversion processes, the literature on the subject mentions two commercial software programs: Aspen Plus and Fluent (version 2021 R2). It is emphasized that better simulation results can be obtained by using these programs simultaneously [1,148]. Few works, including those of the authors of the present article, mention Ansys Chemkin-Pro (version 2021R1) software as an irreplaceable tool for predicting the gaseous products of thermal conversion (Figure 10) [147,149].

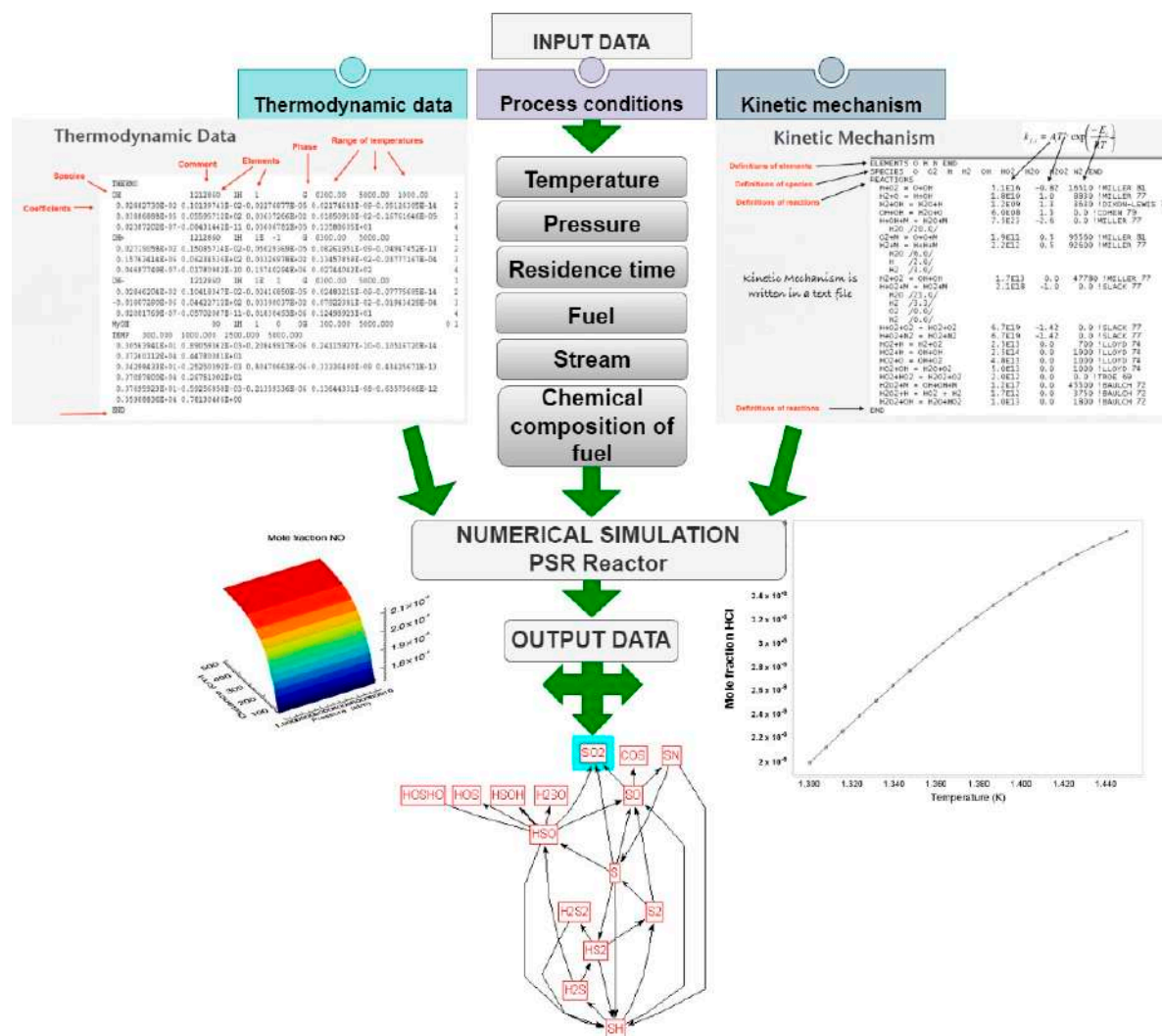


Figure 10. Diagram of procedure for modelling chemical composition of pyrolysis gas using Ansys Chemkin-Pro software [149].

To avoid the complexity of the thermal conversion process, e.g., gasification, and to facilitate the creation of models, some researchers have developed models based on the Aspen Plus process simulator. This involves assessing and analyzing each stage of the process, such as gasification, before integrating it into the global process [149–152]. Each stage of the process, e.g., gasification, can be described and tested in a block before it is integrated into the global process [153,154]. Simulation calculations using this tool are performed using the built-in database of the simulator's physical properties and the database of the properties of the chemical components used in the calculations (e.g., biomass). In addition, custom Fortran or Excel subroutines can be included if necessary [81]. The program uses a sequential modular approach to solve the process diagram module-by-module and calculate the outlet stream properties based on the inlet stream properties for each block. In

modelling, for example, a gasifier in Aspen Plus, the entire process is divided into several sub-processes, including drying and pyrolysis, oxidation and gasification or reduction.

In recent years, there has been a significant increase in the use of Aspen Plus models for thermal conversion processes, particularly gasification, compared to equilibrium models [150–152]. The literature review shows that most researchers rely on non-stoichiometric methods when modelling equilibrium using the Aspen Plus program. On the other hand, stoichiometric equilibrium models are rarely used in the literature, where only numerical models with fewer reactions are described. González-Vázquez et al. [81] compared a non-stoichiometric model and a stoichiometric model, both built using Aspen Plus, to determine their suitability for predicting steady-state biomass gasification efficiency. The simulation results were confirmed by experimental data previously obtained in a semi-pilot atmospheric pressure fluidized bed gasification unit. The authors used Aspen Plus V.8.6 to model biomass gasification and predict synthesis gas. The diagram presents each stage of the process, showing the flows of materials and energy are determined by means of operating blocks.

Models developed with the Ansys Chemkin-Pro tool, which enables accurate modelling of the thermal conversion reaction, e.g., biomass gasification, are definitely popular. The software offers users the ability to develop detailed reaction mechanisms and simulate the thermal decomposition of various raw materials, e.g., biomass, for various process conditions. Additionally, the tool can be integrated with computational fluid dynamics (CFD) models. According to the researchers, Chemkin-Pro is definitely more difficult to use than Aspen Plus, primarily as a consequence of the chemical approach to the analyzed process, based on chemical kinetics, which requires a deeper understanding of the chemical reactions and mechanisms, especially when describing complex biomass gasification processes. Additionally, the technical nature of the software makes it less user-friendly than Aspen Plus, which is designed for a wider range of chemical processes and has a more user-friendly interface. These factors make Chemkin-Pro require a higher level of expertise and effort to effectively utilize its chemical kinetic modelling capabilities in biomass gasification [99].

Examples of the use of Chemkin-Pro software are the simulations carried out by Sieradzka et al. [140] and Slefarski et al. [150]. The authors modelled the chemical composition of the gaseous products of the pyrolysis of fuels derived from waste and identified reaction paths based on kinetic models.

2.4. Validation Techniques of Chemical Kinetics Models in Waste Thermal Conversion Processes

To validate the results of the simulations of the thermal conversion processes of fuels and waste, experimental analyses are primarily used [151,152], including thermogravimetric analysis [111,153–155] with a Fourier transform infrared spectrometer (TG-FTIR) [156–158] and gas chromatography techniques [75,159–161]. Researchers may also compare their results with literature data [52,138].

One of the methods utilized to validate the results obtained by modelling is also statistical analysis employing statistical computing and software [162–164]: MATLAB, ANOVA (tool in OriginPro 2024b) version [165–168] and MS Excel (version 2021).

Statistical approaches [163–165,169], such as response surface methodology (RSM) and Taguchi, are commonly used to optimize experimental parameters (Figure 11). In the RSM optimization process, more series of experiments are usually performed than in the Taguchi method. The RSM model outperforms Taguchi in terms of precision and reliability, while Taguchi's approach is ideal for low-cost and rapid experimental studies. Researchers can choose between the RSM model and Taguchi's approach based on the complexity and financial resources required for their experiments. Several approaches to RSM have been developed over the years. Box Behnken design (BBD) and central composite design (CCD) technologies are the most commonly utilized RSM technologies for catalytic pyrolysis applications. Professor Taguchi developed optimization techniques (Taguchi techniques), which are commonly used to determine the optimal combination of parameters and their

impact on the objective function. Taguchi's optimization approach often uses the variance test, chi-square test and Fisher's exact test [170].

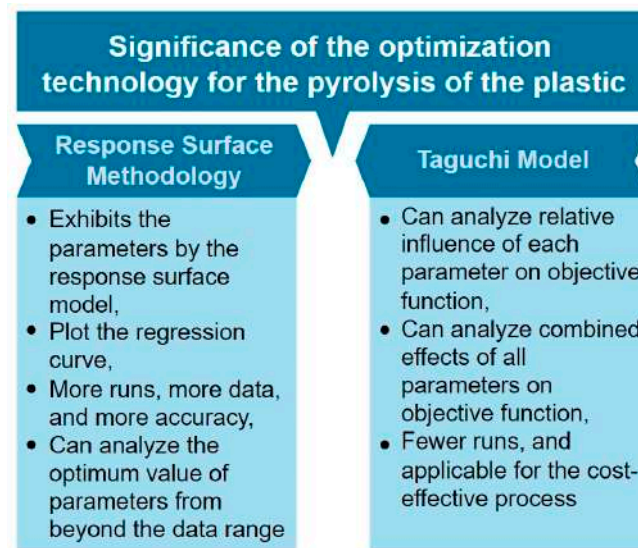


Figure 11. The comparison of response surface methodology and Taguchi method [170].

Regarding the Taguchi method and RSM, the literature has shown that both methods can provide satisfactory optimization results for selected applications, e.g., thermoelectric generators. However, RSM can provide a more comprehensive optimization analysis because it can show the influence of the parameters on the objective function and the interaction between the parameters. Moreover, in RSM, it is possible to visualize the results of the experimental analysis. The Taguchi method is unique in its ability to provide accurate optimization results with a small number of experiments, making it more cost-effective. The comparison and the most important steps of statistical optimization using the Taguchi, ANNOVA and RSM methods are presented in Figures 12 and 13 [165].

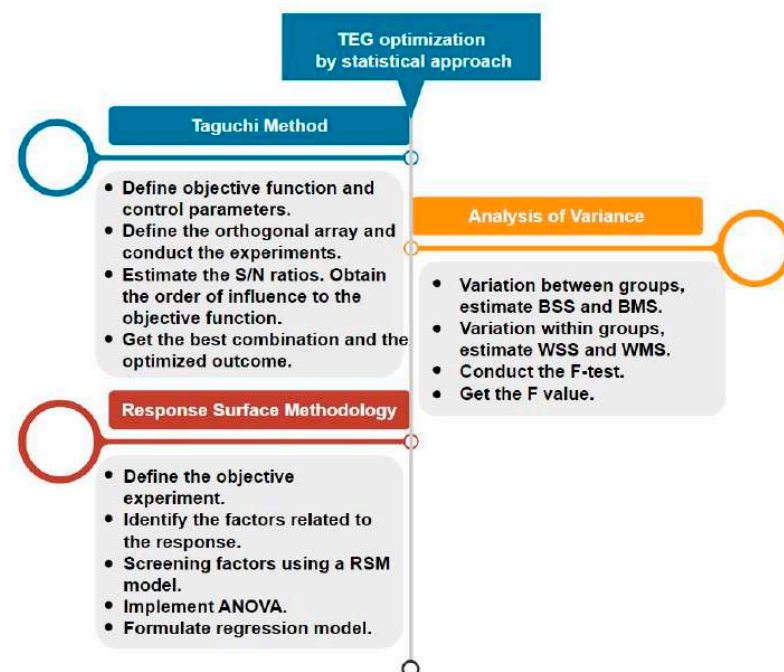


Figure 12. Comparison of optimization approaches for different methods [165].

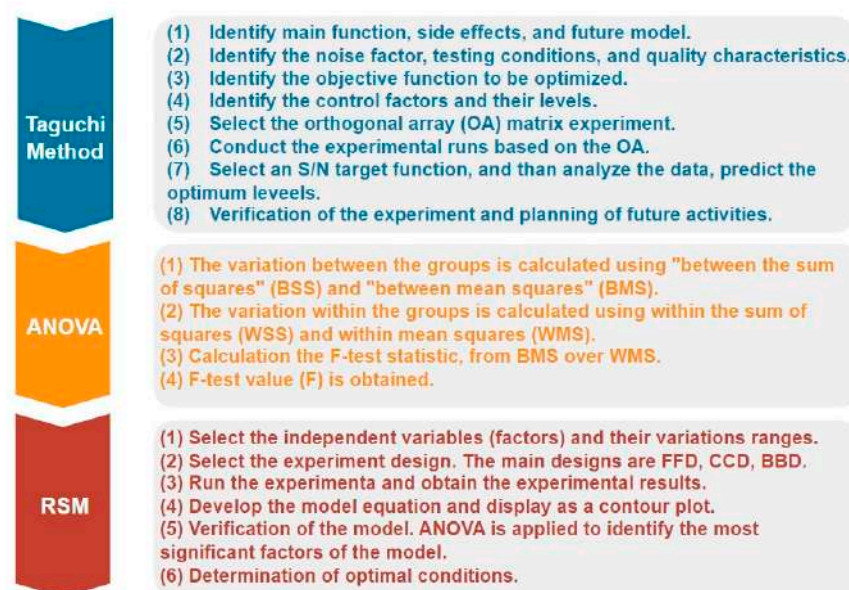


Figure 13. Steps of statistical optimization employing Taguchi, ANNOVA and RSM methods [165].

3. Results

As mentioned earlier, experimental analysis is one of the most frequently used methods to verify the obtained simulation results.

Peters et al. [138] compared the obtained simulation results, described in Section 2.2, with literature data, showing good agreement (Figure 14). Additionally, the authors conducted their pyrolysis experiments to validate the reaction model. The raw material used for the research came from beech wood and was subjected to pyrolysis under precisely defined conditions and at various temperatures. The result of the research was the determination of process efficiency in terms of the received products and their chemical composition. In the final stage, the composition of bio-oil obtained by simulating the pyrolysis of beech wood (moisture 8.9%) was compared with literature data, which showed that beech wood had a lower water content. Comparable proportions were found for organic acids and ketones, while much higher disproportions were obtained for alcohol and aldehyde. In the literature cited by the authors, as much as 44% of the bio-oil was not identified [138].

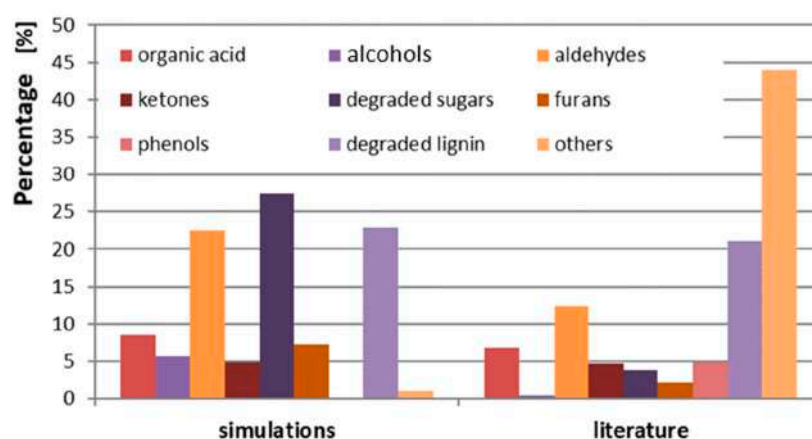


Figure 14. Comparison of the composition of bio-oil from beech wood pyrolysis obtained from simulation and literature data [138].

Ali et al. [171] conducted similar calculations using Aspen Plus software to model the chemical composition of the solid and liquid gasification products of a biomass and coal mixture, receiving results similar to those obtained in experimental studies (Figures 15–17).

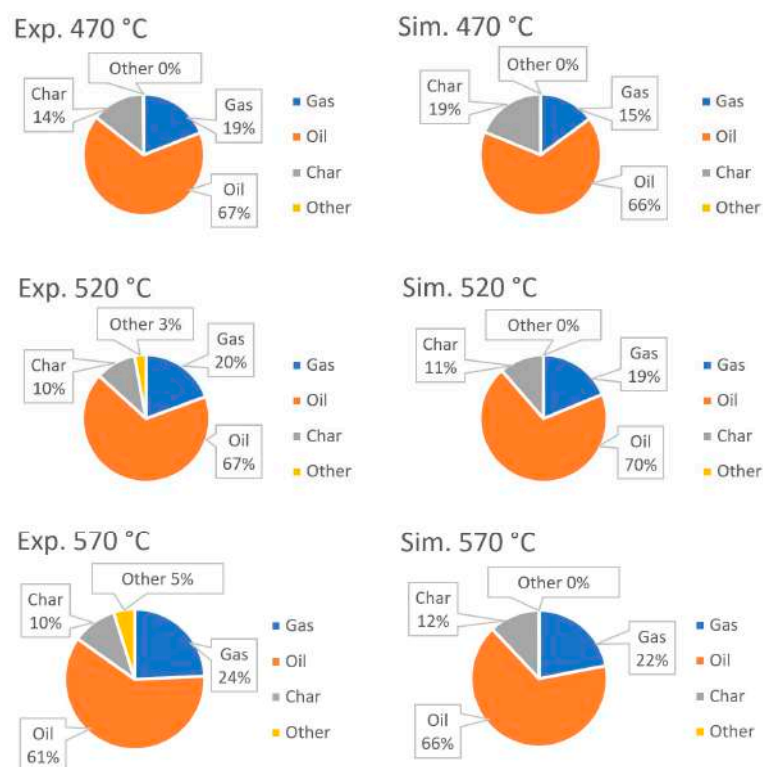


Figure 15. Fraction yield % [171].

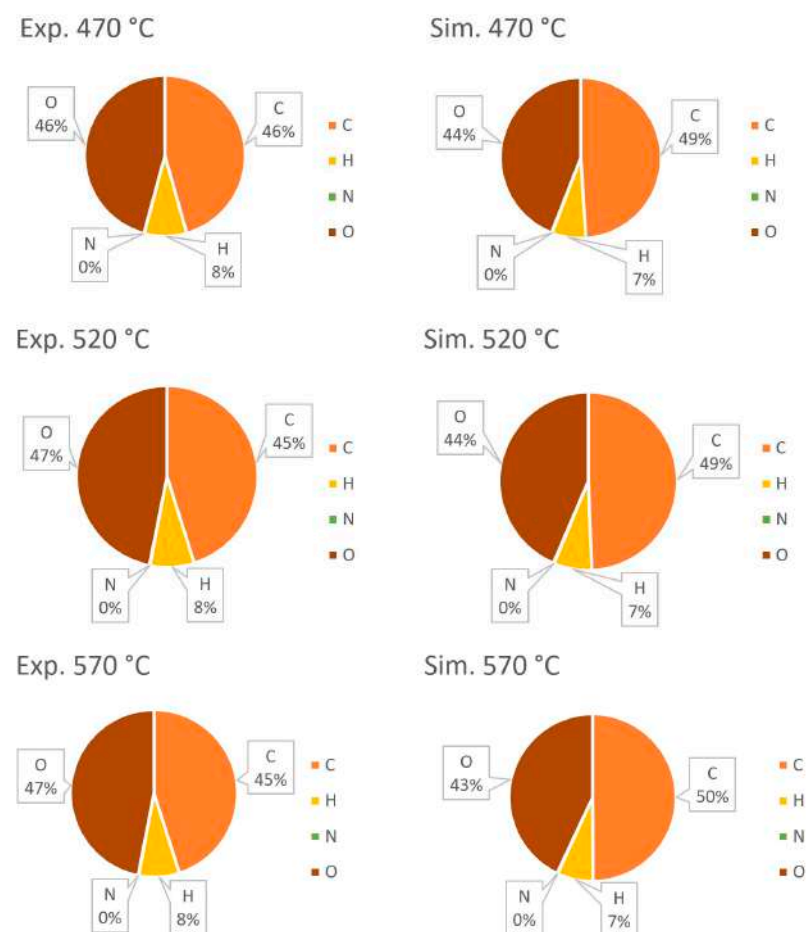


Figure 16. Bio-oil compounds [171].

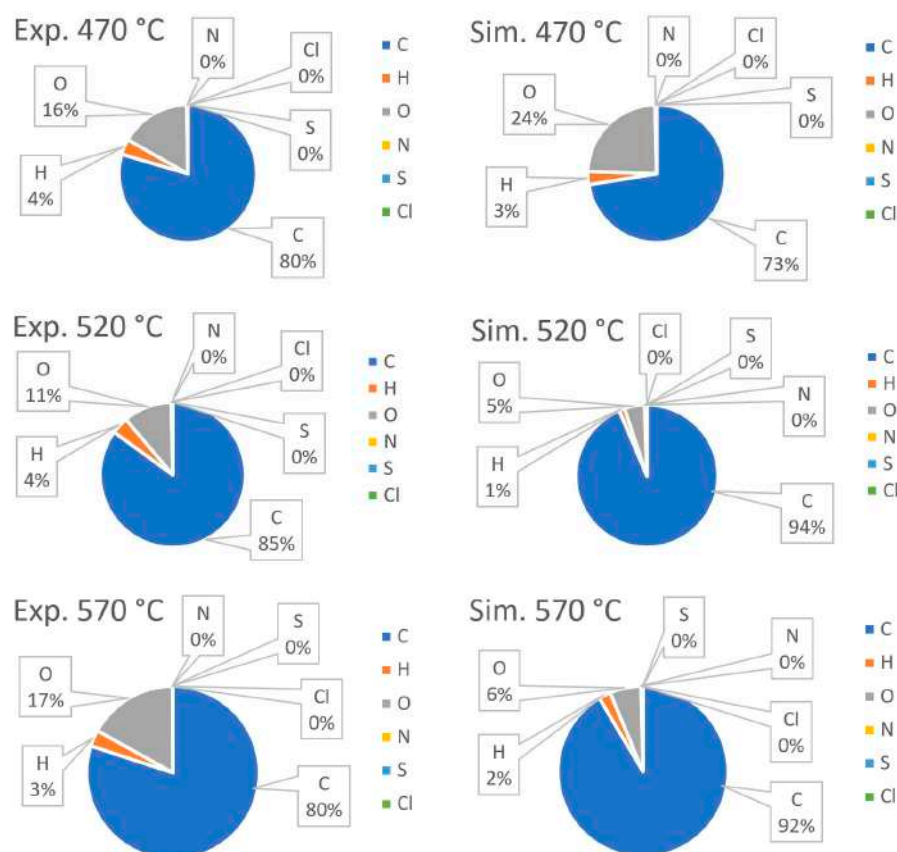


Figure 17. Char composition [171].

4. Discussion

In the era of energy transformation and decarbonization, many efforts are being made worldwide to promote the use of various types of waste as energy sources. These activities are aimed not only at searching for but also promoting sustainable alternatives, thanks to which waste will become a valuable raw material for other processes. Unfortunately, the heterogeneity and varied chemical composition of waste as well as the complexity of the phenomena occurring during thermal conversion make a comprehensive description of the degradation process difficult. This translates into limitations in their widespread use. Computer-simulation methods have been developed in recent years to address these issues, contributing to the intensification of research in the development of numerical models. The main efforts of many research centers around the world are primarily focused on understanding the gas dynamics and chemical mechanisms occurring during the thermal conversion of waste and, in particular, the reaction kinetics. The literature analysis carried out in this article shows that two commercial software products, Aspen Plus and Fluent, are most often used to simulate the processes of the thermal conversion of waste, while only a few works indicate Ansys Chemkin-Pro software as an irreplaceable tool for predicting the gaseous products of thermal conversion [147,149].

To summarize the topic discussed in this article, the following can be noted:

1. The analysis carried out with the use of the VOSviewer software shows that, despite many scientific works published on this topic, there is still a research gap in the issues discussed in the article.
2. The literature on the subject emphasizes that a number of factors are responsible for the proper use of computer simulation methods, and the most important advantage is the ability to simulate phenomena that are difficult or impossible to implement in real conditions.

3. The results of numerical modeling using simplified chemical mechanisms (CFD modeling) describing the combustion process are subject to large errors (due to the long calculation time, simplifications of chemical kinetics are used in the computational procedure, namely reducing the chemistry of methane oxidation to a single-stage mechanism in which combustion products are CO_2 , H_2O , O_2 and N_2), which is why they often do not coincide with actual measurements. The assumption of a simple combustion mechanism in the calculations results in significant discrepancies with the measurement results.
4. Due to the possibility to create a multi-stage, complex model in the ANSYS Chemkin-Pro program, which does not use simplifications in thermodynamics and chemical kinetics, various waste thermal processing processes can be modeled with high accuracy.
5. The cost of building a model is often much lower than conducting experimental research, resulting in significant savings in time and money.
6. Computer simulations also have several disadvantages, the most important of which is the possibility of making an error when creating a model that omits parameters and chemical reactions that are important from the point of view of the analyzed process.
7. Moreover, numerous works indicate difficulties and errors when interpreting the obtained simulation results. The above-mentioned defects are the responsibility of humans, who may not only incorrectly formulate the simulated problem and adjust the tool but may also draw incorrect conclusions from the performed simulations.
8. It is crucial to validate the developed model and verify the obtained calculations through experimental means using statistical analysis (e.g., MATLAB, ANOVA) or based on literature data. Without such validation, the results of the model calculations remain hypothetical.
9. The issue of managing environmentally burdensome gaseous products of thermal conversion of calorific waste is of an applied nature, as evidenced by the interest of both entrepreneurs from the waste and metallurgical industries. However, this direction requires extensive theoretical studies in the analysis of chemical mechanisms.
10. Knowledge of chemical mechanisms describing the process of combustion or co-combustion of gases from the thermal conversion of waste will create the possibility of their energy utilization.
11. Providing comprehensive knowledge about combustion kinetics will also enable taking appropriate actions to manage gases after thermal conversion of waste while maintaining the proper operation of the heating chamber and minimizing pollution.
12. Currently, it is particularly important and problematic to properly identify the chemical composition of exhaust gases while, at the same time, focusing on activities aimed at minimizing harmful pollutants, such as PAHs.

The analysis conducted in this article indicates enormous progress in modelling the processes of the thermal conversion of waste. This suggests that numerical simulations will likely replace costly experimental research in the future. Nonetheless, it is important to consider that, as the number of phenomena to be modelled increases, the accuracy of the model also increases, resulting in a better reflection of reality, but, at the same time, requiring a longer calculation time and greater computing power, leading to higher costs. Moreover, thermal management of waste towards the recovery of valuable products, such as pyrolysis gas, biochar and condensate, as is the case in the pyrolysis process, is an additional opportunity to improve energy efficiency. Using the potential of post-process gases, especially gases from the pyrolysis process, e.g., of biomass, will have an economic impact, contributing to lower fuel consumption.

5. Conclusions

To sum up, it is important to note that, despite the disadvantages and difficulties associated with creating advanced simulation projects, they are an integral element of the development of all industries. The use of simulation in thermal waste conversion processes is an opportunity to employ them on a wider scale, thanks to a better understanding

of the phenomena occurring during their degradation, both gasodynamic and kinetic. The analysis performed using the VOSviewer software indicates the need to develop mathematical models used when modeling thermal processes. Reducing the expenditure that would be necessary for extensive experimental research will contribute to a faster transformation of a linear economy into a circular economy that promotes the efficient use of waste.

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Analysis of chemical mechanisms of the formation of environmentally harmful gas combustion products from waste pyrolysis

Analiza mechanizmów chemicznych powstawania uciążliwych dla środowiska produktów spalania gazu z pirolizy odpadów

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Computer simulations of the combustion process of pyrolytic gases from RDF pyrolysis and a mixture of polypropylene with pine chips as well as natural gas were carried out. The effect of temp. and residence time on the compn. of combustion products was examined. Calcns. were carried out using the ANSYS Chemkin PRO program, and the input data for the calcns. were taken from exptl. studies carried out at the test stand. Computer simulations showed that the chem. compn. of gases from the combustion of pyrolytic gases, as a function of variable combustion process parameters, such as temp. and residence time of the reagents in the highest temp. zone, is qual. similar to the compn. of exhaust gases from the combustion of natural gas.

Keywords: metallurgical industry, waste pyrolysis, thermal conversion products

Przedstawiono wyniki symulacji komputerowych wpływu wybranych parametrów procesu termicznej konwersji, takich jak temperatura i czas przebywania, na mechanizm powstawania uciążliwych dla środowiska gazowych produktów. Analizie poddano gazy pochodzące z pirolizy RDF (refuse derived fuel) oraz mieszaniny zrębków sosnowych z polipropylenem. Uzyskane wyniki obliczeń dla wybranych związków porównano z danymi dla gazu ziemnego. Mogą one znaleźć praktyczne zastosowanie w przemyśle hutniczym, jako podstawa do rozważań nad energetycznym wykorzystaniem gazowych produktów pirolizy do opalania pieców grzewczych jako substytutu gazu ziemnego.

Słowa kluczowe: przemysł hutniczy, piroliza odpadów, produkty termicznej konwersji

Problematyka powstawania uciążliwych dla środowiska gazowych produktów wpisuje się w aktualne wyzwania środowiskowe, przed którymi stoją najbardziej energochłonne gałęzie przemysłu, takie jak przemysł żelaza i stali. Szansą na poprawę efektywności energetycznej zmierzającej do obniżenia zużycia paliwa, a tym samym zmniejszenia emisji zanieczyszczeń, zwłaszcza CO₂, jest wykorzystanie potencjału gazów pochodzących z termicznej konwersji odpadów, a w szczególności gazu pirolitycznego¹⁾. Jak wskazują liczne źródła literaturowe zagospodarowanie uciążliwych dla środowiska gazowych produktów termicz-

nej konwersji cieszy się zainteresowaniem nie tylko przedsiębiorców branży odpadowej, ale również metalurgicznej²⁾.

Zasadniczym problemem ograniczającym energetyczne wykorzystanie gazu pirolitycznego na szeroką skalę jest złożony mechanizm chemiczny jego spalania i niezbadane szczegółowo konsekwencje środowiskowe. Dodatkowo analizę procesu utrudniają zarówno warunki spalania, jak i rodzaj spalanego paliwa, a w szczególności zróżnicowany skład chemiczny gazów pochodzących z termicznej konwersji odpadów^{3, 4)}. Dogłębne rozpoznanie mechanizmów chemicznych opisujących proces spalania lub współspala-



Mgr inż. Magdalena SKRZYNIARZ (ORCID 0000-0002-8577-021X) w roku 2017 ukończyła studia na Wydziale Inżynierii Produkcji i Technologii Materiałów Politechniki Częstochowskiej i jednocześnie rozpoczęła doktorat na tym samym wydziale. Zajmuje się zagadnieniem dotyczącym spalania paliw i odpadów oraz ich racjonalnym gospodarowaniem, z uwzględnieniem ochrony środowiska.



Dr inż. Jakub RZĄCKI (ORCID 0000-0002-4354-525X) w roku 2009 ukończył studia na Wydziale Inżynierii Procesowej, Materiałowej i Fizyki Stosowanej Politechniki Częstochowskiej. W 2013 r. uzyskał stopień doktora nauk fizycznych na Wydziale Fizyki i Informatyki Stosowanej Uniwersytetu Łódzkiego. Jest adiunktem w Katedrze Fizyki Politechniki Częstochowskiej. Specjalność – fizyka ciała stałego.

* Adres do korespondencji:

Wydział Inżynierii Produkcji i Technologii Materiałów, Politechnika Częstochowska, al. Armii Krajowej 19, 42-201 Częstochowa, tel.: (34) 325-07-70, e-mail: magdalena.skrzyniarz@pcz.pl

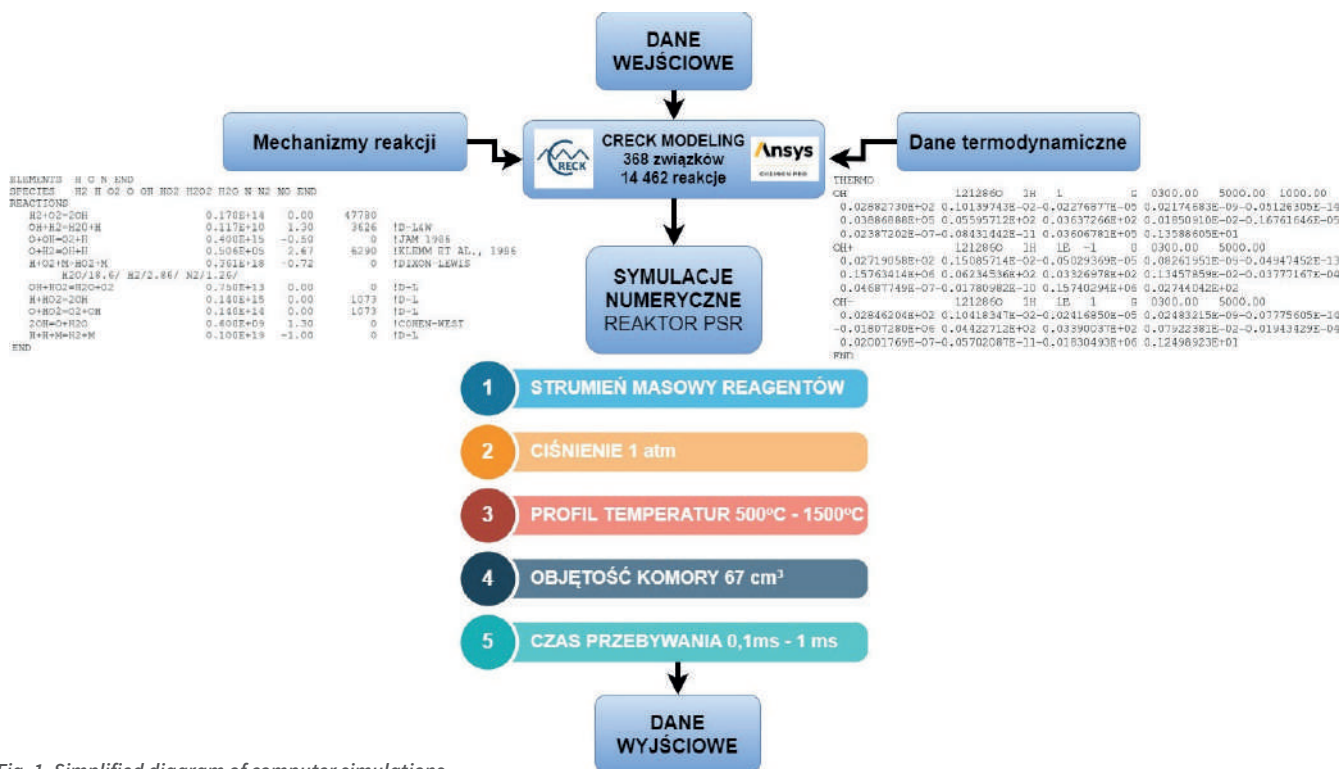


Fig. 1. Simplified diagram of computer simulations

Rys. 1. Uproszczony schemat prowadzonych symulacji komputerowych

nia omawianych gazów procesowych i ich mieszanin nie tylko uzupełni lukę literaturową w zakresie identyfikacji składu chemicznego spalin, ale również umożliwi podjęcie stosownych działań zmierzających do minimalizacji powstawania szkodliwych substancji zanieczyszczających⁵⁻⁷. Szczególnej uwagi wymagają sytuacje, w których w urządzeniach dochodzi do obniżenia sprawności spalania paliwa, niewłaściwego wymieszania reagentów lub nadmiernego schłodzenia płomienia przed zakończeniem spalania, co prowadzi do niedoboru tlenu. Konsekwencją spalania w warunkach niedoboru tlenu jest emisja niedopalonych węglowodorów oraz sadzy, które mogą stanowić zagrożenie związane z wybuchem w przewodach spaliniowych⁸.

Celem pracy była analiza mechanizmów chemicznych w funkcji zmiennej temperatury i czasu przebywania, tworzenia i rozkładu wybranych zanieczyszczeń gazowych powstających podczas spalania gazów pochodzących z pirolizy odpadów. Badania były wstępem do analizy mechanizmów chemicznych powstawania i rozkładu wybranych produktów spalania gazu pirolitycznego w wysokotemperaturowej komorze grzewczej.

Część badawcza

Metody obliczeniowe

Obliczenia wykonano z wykorzystaniem oprogramowania komputerowego ANSYS Chemkin PRO (ver. 2021R1), w ramach licencji usługi chmurowej w sieci Pionier. Mechanizm chemiczny został zaczerpnięty z bazy danych Creck Modeling i obejmował 368 związków oraz

14 462 reakcje⁹. Obliczenia przeprowadzono dla reaktora o stałej objętości z idealnym wymieszaniem reagentów PSR (*perfectly stirred reactor*). Dane wejściowe do obliczeń zaczerpnięto z badań eksperymentalnych przeprowadzonych na stanowisku badawczym opisanym w pracy⁸, dla stałej wartości stosunku nadmiaru powietrza $\lambda = 1,05$. Uproszczony schemat prowadzonych obliczeń przedstawiono na rys. 1.

Analizie poddano dwa gazy pirolityczne uzyskane z procesu pirolizy paliwa alternatywnego RDF oraz mieszaniny zrębków sosnowych z polipropylenem (ZS+PP, mieszanina 70% sosna, 30% PP) oraz dla porównania gaz ziemny. Składy gazów zostały zamieszczone w tabeli.

Table. Chemical composition of analyzed gases

Tabela. Skład chemiczny analizowanych gazów

Składnik	Rodzaj gazu		
	Gaz ziemny, % ⁽⁸⁾	Gaz pirolityczny z RDF, % ⁽¹⁰⁾	Gaz pirolityczny z ZS+PP, % ⁽¹¹⁾
H ₂	-	12,37	7,94
CO	-	29,69	26,43
CH ₄	96,65	17,83	23,15
CO ₂	0,32	11,89	29,44
N ₂	1,20	-	-
C ₂ H ₄	-	13,84	1,47
C ₂ H ₆	1,84	4,03	2,88
C ₃ H ₈	-	0,43	1,08
C ₃ H ₆	-	7,34	5,56
LHV, MJ/m ³	34,40	29,94	24,20

LHV (lower heating value) – dolna wartość opałowa

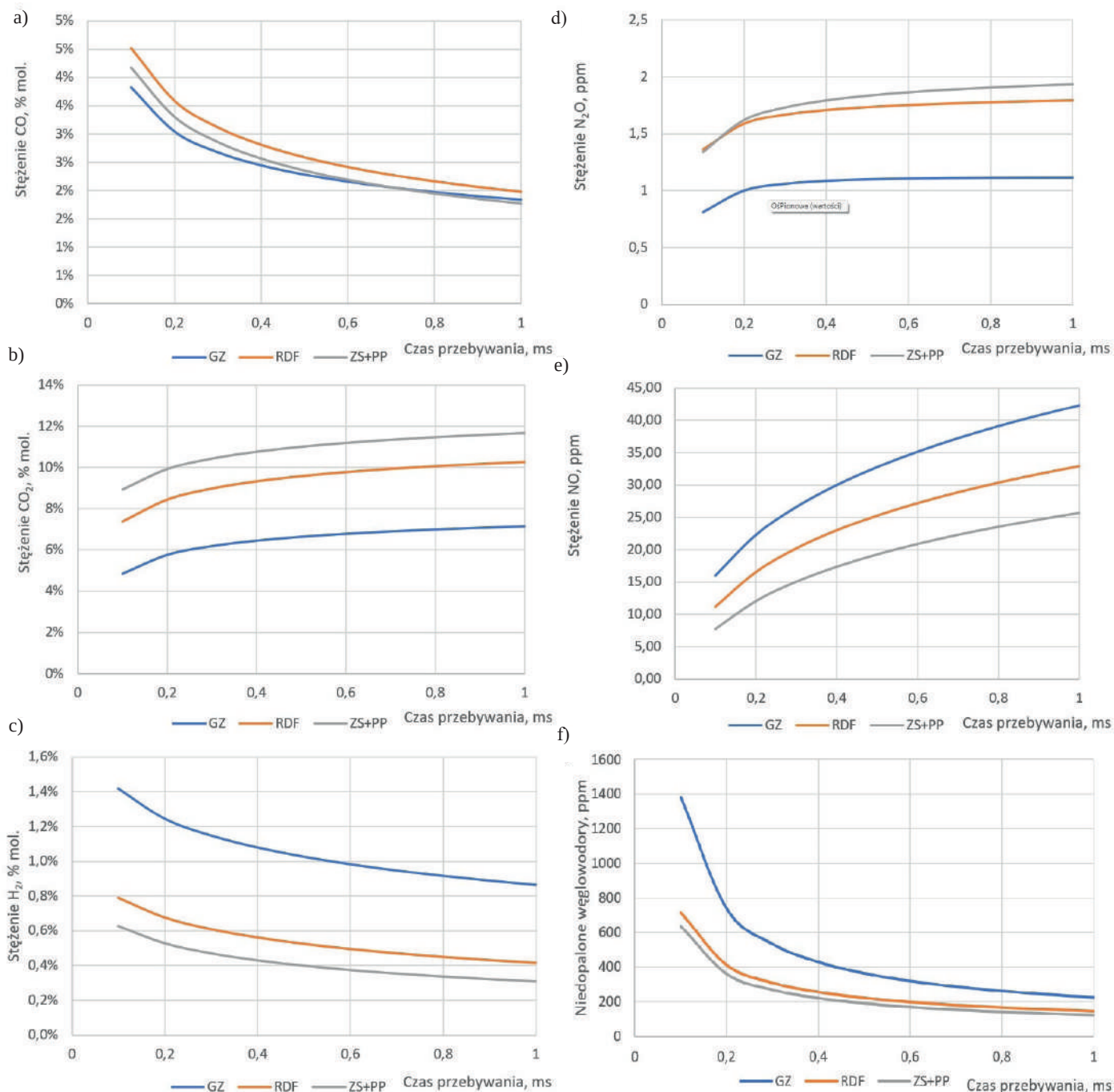


Fig. 2. Molar concentration as a function of residence time of: a) CO, b) CO₂, c) H₂, d) N₂O, e) NO, and f) unburned hydrocarbon

Rys. 2. Stężenie molowe w funkcji czasu przebywania: a) CO, b) CO₂, c) H₂, d) N₂O, e) NO i f) niedopalonych węglowodorów

Wyniki symulacji

Wyniki symulacji wpływu czasu przebywania na powstawanie CO, CO₂, H₂, N₂O, NO i niedopalonych węglowodorów przedstawiono na rys. 2, a wpływ temperatury na rys. 3. Z symulacji komputerowych wynika, że skład spalin powstałych ze spalania gazów pirolitycznych był pod względem jakościowym zbliżony do składu spalin z gazu ziemnego. W funkcji czasu przebywania i stałej temp. 1500°C obserwowano wzrost stężenia NO, N₂O i CO₂ dla wszystkich analizowanych gazów. Największe stężenie NO było w gazach ze spalania gazu ziemnego i dla czasu przebywania 1 ms wyniosło 42 ppm, a najmniejsze w gazach

ze spalania gazu z pirolizy ZS+PP i wyniosło 25 ppm. Dwukrotnie większe stężenie należy tłumaczyć m.in. obecnością azotu cząsteczkowego w składzie gazu ziemnego. Odwrotną sytuację obserwowano dla N₂O, którego stężenie w gazach ze spalania gazu ziemnego było mniejsze niż w gazach ze spalania gazów pirolitycznych, co może mieć związek z mechanizmem chemicznym powstawania i rozkładu tlenków azotu. Najmniejsze różnice w wartościach stężeń obserwowano dla CO, a największe dla H₂. W przypadku takich związków, jak CO₂, N₂O i NO ich stężenie molowe roso wraz ze wzrostem czasu przebywania. Zmniejszenie stężenia molowego zaobserwowane

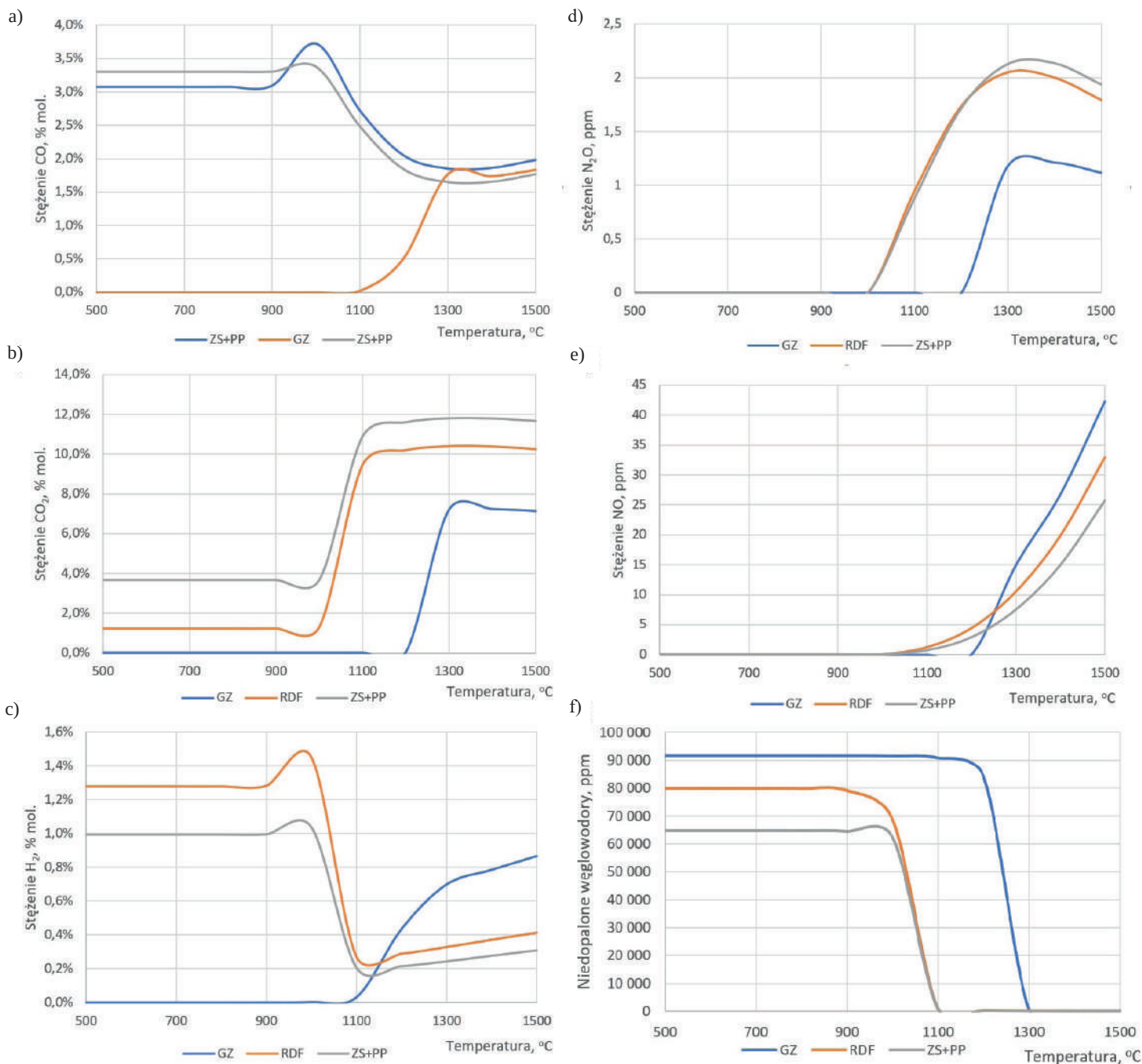


Fig. 3. Molar concentration as a function of temperature of: a) CO, b) CO₂, c) H₂, d) N₂O, e) NO, and f) unburned hydrocarbon

Rys. 3. Stężenie molowe w funkcji temperatury: a) CO, b) CO₂, c) H₂, d) N₂O, e) NO i f) niedopalonych węglowodorów

w przypadku CO i H₂ było związane z ich dopalaniem występującym wraz ze wzrostem czasu przebywania.

Dla wszystkich analizowanych gazów obserwowano wzrost stężeń CO₂, N₂O i NO w funkcji temperatury i stałego czasu przebywania 1 ms. Wraz ze wzrostem temperatury spalania powyżej 1100 °C obserwowano gwałtowny wzrost stężeń NO dla wszystkich trzech gazów, będący skutkiem mechanizmu Zeldowicza, który odpowiada za formowanie NO w wysokich temperaturach (powyżej 1250 °C)¹².

Odmianą sytuację obserwowano dla stężenia N₂O, które w gazach ze spalania gazu ziemnego było najmniejsze w porównaniu z dwoma gazami pirolitycznymi. Gwałtowny

wzrost stężenia tlenku diazotu powyżej 1000 °C, a następnie spadek powyżej 1300 °C można wytłumaczyć reakcjami rozkładu i tworzenia azotu (1) i (2)¹²:



Ditlenek azotu powstaje wskutek odwrotnej reakcji (1), a reakcja (2) jest źródłem powstawania NO. Najmniejsze różnice w wartościach stężeń zaobserwowano dla NO, największe zaś dla H₂.

W przypadku takich związków, jak CO₂, N₂O i NO ich stężenie molowe w gazie rosło wraz ze wzrostem tempe-

ratury. Spadek stężenia molowego obserwowano w przypadku CO i H₂ (tylko dla gazów pirolitycznych), co było związane z wysoką zawartością wodoru i węglowodorów w składzie paliw, a następnie ich stopniowym dopalaniem w miarę wzrostu temperatury.

Dla niedopalonych węglowodorów (rys. 2f i 3f) symulacje wykazały, że wraz ze wzrostem temperatury i wydłużeniem czasu przebywania ich stężenie dla wszystkich analizowanych gazów malało. Na uwagę zasługuje spostrzeżenie, że podczas spalania gazu ziemnego w niższych temperaturach (ok. 1200°C) w składzie atmosfery gazowej pozostawało więcej niedopalonych węglowodorów w porównaniu z gazami pirolitycznymi. W przypadku potwierdzenia takiego zachowania w warunkach procesowych może to stanowić istotny argument przy podejmowaniu decyzji o energetycznym wykorzystaniu gazów pirolitycznych.

Podsumowanie

Zróznicowany skład chemiczny gazów pochodzących z termicznej konwersji odpadów oraz złożony mechanizm chemiczny procesu spalania ograniczają ich energetyczne wykorzystanie na szeroką skalę.

Poznanie i odpowiednia kontrola mechanizmów chemicznych formowania i rozkładu uciążliwych dla środowiska związków może przyczynić się do efektywnego zagospodarowania gazowych produktów z pirolizy odpadów, z uwzględnieniem konsekwencji środowiskowych.

Przeprowadzone symulacje komputerowe wykazały, że skład chemiczny gazów powstałych ze spalania gazów pirolitycznych w funkcji zmiennych parametrów procesu spalania, takich jak temperatura i czas przebywania reagentów w strefie najwyższych temperatur, jest pod względem jakościowym zbliżony do składu spalin ze spalania gazu ziemnego.

Wraz ze wzrostem temperatury i czasu przebywania obserwowano wzrost stężeń CO₂, N₂O i NO dla wszystkich analizowanych gazów. Największe stężenie NO obserwowano podczas spalania gazu ziemnego, które dla czasu przebywania 1 ms wynosiło 42 ppm, a najmniejsze (25 ppm) było ze spalania gazu z pirolizy ZS+PP.

Dłuższy czas przebywania i wyższa temperatura spalania wpływają na zmniejszenie stężenia niedopalonych węglowodorów w spalinach dla wszystkich analizowanych gazów.

Przedstawione wyniki mogą znaleźć zainteresowanie zakładów hutniczych w zakresie energetycznego wykorzystania gazowych produktów pirolizy do opalania pieców grzewczych jako substytutu gazu ziemnego.

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Article

Prediction of Chemical Composition of Gas Combustion Products from Thermal Waste Conversion

Magdalena Skrzyniarz , Sławomir Morel and Jakub Rzącki 

Faculty of Production Engineering and Materials Technology, Czestochowa University of Technology,
19 Armii Krajowej Ave., 42-200 Czestochowa, Poland; slawomir.morel@pcz.pl (S.M.); jakub.rzacki@pcz.pl (J.R.)

* Correspondence: magdalena.skrzyniarz@pcz.pl; Tel.: +48-(34)-3250773

Abstract: The current global energy crisis is driving the need to search for alternative raw materials and fuels that will be able to ensure the continuity of strategic industries, such as the steel industry. A chance to reduce the consumption of traditional fuels (e.g., natural gas) is to utilise the potential of gases from the thermal conversion of waste, and, in particular, pyrolysis gas. Unfortunately, despite its high calorific value, this gas is not always suitable for direct, energy-related use. The limitation is the type of waste subjected to pyrolysis, particularly plastics, rubber and textiles. Due to the above, this article proposes the co-combustion of pyrolysis gas in a ratio of 1:10 with natural gas in a pusher reheating furnace employed to heat the charge before forming. The chemical composition of flue gases generated during the combustion of natural gas alone and co-combustion with pyrolysis gas from various wastes was modelled, namely, two types of refuse-derived fuel (RDF) waste, a mixture of *pine* chips with polypropylene and a mixture of *alder* chips with polypropylene. The calculations were performed using Ansys Chemkin-Pro software (ver. 2021 R1). The performed computer simulations showed that the addition of pyrolysis gas for most of the analysed variants did not significantly affect the chemical composition of the flue gases. For the gases from the pyrolysis of biomass waste with the addition of polypropylene (PP), higher concentrations of CO and H₂ and unburned hydrocarbons were observed than for the other mixtures. The reason for the observed differences was explained by conducting a formation path analysis and a sensitivity analysis for the selected combustion products.



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Keywords: pusher furnace; waste; pyrolysis gas; sensitivity analysis; Ansys Chemkin-Pro

1. Introduction

One of the main branches of industry, the steel industry, is of key importance for the economies of all countries; at the same time, it is one of the most energy-intensive and highest emission-producing industries [1,2]. Despite this, its products are among the basic materials used by most sectors of the world economy. The price and quality of these products largely determine the level of competitiveness in world markets [3,4]. In order to meet high economic and ecological requirements, the Polish steel industry is forced to modernise its production processes. It is particularly important to search for new methods of reducing pollutant emissions for all processes in technological chains; this applies primarily to steel mills with a full production cycle [5–7]. The currently used iron and steel production technologies, despite many modern investments, are still characterised by a negative impact on the environment, which especially concerns CO₂ emissions and energy consumption [8,9]. Therefore, new solutions are sought, which include innovative technologies developed within international programmes for reducing CO₂ emissions. Noteworthy are the optimisation activities carried out in many global steel mills, which result not only in reduced fuel consumption, but also in reduced pollutant emissions. An example of such a solution is the appropriate selection of combustion process parameters (in particular, the excess air ratio and the temperature of heated air), the use of low-emission

burners and the management of so-called production gases in the combustion process, especially those rich in hydrogen [10–13].

The steel industry, apart from high pollutant emissions, is also characterised by high energy intensity [14–17]. Considering the fact that improving energy efficiency is one of the priorities of the EU's energy policy, Poland has also declared a national target in this respect, i.e., 23% by 2030 in relation to the primary energy forecasts from 2007 [18,19]. The potential for improving energy efficiency covers almost the entire Polish economy, but significant benefits are seen in improving energy-intensive processes in steel production.

An opportunity to improve energy efficiency, aimed at reducing fuel consumption, is to utilise the potential of post-process gases, such as coke oven gas and gases from thermal conversion of waste [20,21]. Particular attention should be paid to the gaseous products of the pyrolysis process, namely pyrolysis gas, which currently has no reliable or permanent method of utilisation [22–24]. Depending on the material subjected to pyrolysis, pyrolysis gas mainly consists of compounds such as methane, hydrogen, carbon dioxide, carbon monoxide and C2–C6 hydrocarbons [25–27]. The yield of pyrolysis gas can even reach over 50% and depends on both the properties of the processed material and the process conditions, in particular the temperature and residence time [28–30].

This article presents a promising approach to the energy use of thermal conversion gases, which is based on the possibility of co-combusting pyrolysis gas (from biomass, PP and RDF) with natural gas in a pusher-type metallurgical furnace.

1.1. Energy Potential of Thermal Waste Conversion Products

1.1.1. Gaseous Products

Considering the depletion of fossil fuel resources, all types of waste are becoming an attractive and ecological alternative for obtaining energy. The ongoing energy crisis is deepening as a consequence of the geopolitical situation in Europe and the Middle East. Society and the largest economies of the world face the challenge of creating a new, reliable and stable source of energy that will not exploit the earth's fossil fuel resources [31]. Numerous scientific publications prove [32–36] that the pyrolysis process, depending on the material subjected to thermal treatment, can be a source of valuable fuels and, in particular, pyrolysis gas [37–40]. The obtained gaseous products are rich in gases such as H₂, CH₄ and CO (Table 1), which are the basic components of fossil fuels [41].

Table 1. Composition of pyrolysis gas obtained from various wastes (literature data).

Compound (vol%)	H ₂	CO	CO ₂	CH ₄	C ₂ –C ₅	Calorific Value (MJ/m ³)	Ref.
LDPE:SS	25.57	2.71	4.14	46.31	21.27	43.82	[31]
Tyre	21.50	5.10	26.20	17.30	29.90	30.30	[42]
RDF	29.40	11.30	13.20	32.90	7.20	22.80	[43]
RDF	12.37	29.69	11.89	17.83	25.70	29.94	[44]
Biomass	0.02	6.70	6.80	0.69	0.91	-	[45]

LDPE—low-density polyethylene rejects; SS—sewage sludge.

The literature data indicate that pyrolysis gas may differ significantly in composition and calorific value, depending on the material subjected to pyrolysis. The calorific value of the obtained gas fraction may range from 10 to 15 MJ/m³ for gases from biomass pyrolysis and reach a value of over 40 MJ/m³ for gas from the pyrolysis of various plastics. Considering the calorific value of natural gas, which is about 35 MJ/m³, and the calorific value of coke oven gas, which reaches approximately 17 MJ/m³, it can be stated that gaseous pyrolysis products can be a good alternative to the combustion of natural gas and coke oven gas after meeting appropriate conditions [24,46].

1.1.2. Solid Products

The key parameters that affect the properties of solid pyrolysis products are the process temperature, heating rate, residence time, additives and catalysts, in addition to

the composition of the basic raw material that is subjected to pyrolysis. Biochar is very often characterised by a porous structure, high absorption properties and stable chemical properties [47]. Biochar consists mainly of coal, ash, volatile substances and water, with ash constituting the largest part, namely over 80%. Depending on the input material, transition metal compounds may be present in the ash, which have very good absorption capacities [48]. Example compositions of biochar are presented in Table 2.

Table 2. Examples of compositions of solid fractions from various materials (literature data).

Material (wt%)	C	H	N	S	O	Calorific Value (MJ/kg)	Ref.
Tyre waste	80.82	1.46	0.53	2.41	-	30.0	[42]
Pear wood	84.00	1.91	0.65	0.01	7.26	33.55	[49]
Virginia mallow	49.90	5.69	0.39	0.10	37.42	18.51	[50]

As presented in Table 2, the main component of the solid fraction is carbon. Its content ranges from nearly 60% for Virginia mallow to over 80% for pear wood and tyre waste. The conditions of the pyrolysis process have a huge impact on the content of the carbon element in biochar. The higher the temperature, the more carbon is bound in the solid fraction. The carbon content in the solid product is closely related to its calorific value; the higher its content, the higher the calorific value. The calorific value of biochar ranges from 18 to 36 MJ/kg, where, for comparison, the calorific value of hard coal is in the range of 22–24 MJ/kg, the calorific value of brown coal is 7.5–21 MJ/kg and that of eco-pea coal is 24–26 MJ/kg [46,47,51].

1.1.3. Liquid Products

The third product, in addition to the gaseous and solid fractions, produced in the pyrolysis process is pyrolysis oil. It is characterised by a high content of aromatic hydrocarbons. Depending on the material subjected to pyrolysis, the optimum temperature that allows the process to be directed towards the production of pyrolysis oil is about 500 °C [42]. The type of input material has the greatest influence on the chemical composition and calorific value of the oil fraction (Table 3) [22].

Table 3. Composition of liquid fraction from various wastes (literature data).

Material	Elemental Composition (wt%)						HHV (MJ/kg)	Ref.
	N	C	H	O	Cl	S		
PE	0.30	84.28	13.79	1.63	n.d.	n.d.	48.06	[41]
PVC	0.11	56.88	8.76	34.09	0.16	n.d.	18.45	
LDPE:SS	0.60	80.40	14.50	n.d.	n.d.	<0.3	37.65	[31]
Olive oil residue	1.64	70.24	8.42	19.70	n.d.	n.d.	32.36	[52]
Waste tyres	0.60	88.10	10.70	0.06	n.d.	0.60	43.30	[53]

PE—polyethylene; PVC—polyvinylchloride; LDPE—low-density polyethylene waste; SS—sewage sludge.

As can be seen, the calorific value of all the pyrolysis oils listed in Table 3 differs within a wide range. The lowest value was obtained from PVC, namely 18.45 MJ/kg, while the highest was 48.06 from PE, which exceeds the calorific value of crude oil [31]. The organic fraction of the liquid phase contains chemical substances such as ethylbenzene, styrene and toluene, whose calorific value in the pure form reaches 33–40 MJ/kg, which positively affects the high calorific value of the obtained pyrolysis oils [54].

1.2. Utilisation of Gases from Thermal Conversion

As shown above in Tables 1–3, the energy potential of thermal waste conversion products is very high. In many cases, the calorific value of the obtained products exceeds the calorific values of fossil fuels. The interest in the utilisation of gaseous thermal waste conversion products is evidenced by numerous scientific publications [55–58]. Hossain et al. [24]

conducted studies of pyrolysis gas combustion in spark-ignition engines. The obtained results showed that it is possible to obtain the same power as when operating on natural gas, but the engine operation was less stable. The key parameter may also be the engine failure rate, which cannot be precisely determined after 100 h of engine operation on a given fuel. Liu et al. [23] subjected sewage sludge to pyrolysis. They determined that the optimal conditions for the process in their case were a temperature of 450 °C and residence time of 30 min. Such parameters allowed them to achieve a yield of about 52.36% for biochar and 46.40% for pyrolysis gas. The researchers proposed using the resulting pyrolysis gas for direct combustion, and the resulting flue gases could be utilised to dry wet sewage sludge or generate steam. Mounair et al. [22] analysed the use of the energy potential of pyrolysis gas obtained from used tyres. The authors proposed utilising the obtained gas to power the pyrolysis process in order to reduce or completely eliminate the need to supply a flammable medium from outside. The researchers found that pyrolysis gas has a huge energy potential, but additional attention should be paid to the quality of the obtained products, the level of sulphur content and detailed monitoring of pollutant emissions. Pessoa Filho et al. [59] aimed to determine the optimal conditions of the pyrolysis process to obtain a high share of pyrolysis gas from the pyrolysis of solid plastic waste, and then simulated the combustion of the gas. The authors proposed a burner concept that had an impact on the reduction of CO_x and C_xH_y emissions. The obtained results showed that the lower calorific values of the received gases were similar to the values of commercial combustible gases. Additionally, the orientation of pyrolysis towards gas production and the selection of appropriate parameters allowed 98.01 vol% pyrolysis gas to be obtained from HDPE pyrolysis. As proven by numerous works [60–63], the yield of individual products in the pyrolysis and gasification process depends on a number of different parameters, such as the process temperature, pressure, catalysts, residence time and the material subjected to thermal decomposition [59]. The yield of individual pyrolysis products for selected wastes is presented in Table 4.

Table 4. Yield of pyrolysis products for selected waste.

Material	Product Yield (vol%)			Ref.
	Biochar	Bio-Oil	Gas	
Pear wood	30.10	21.10	34.40	[49]
Tyre	44.20	38.30	17.50	[42]
Sewage sludge	54.53	18.62	26.85	[64]
HDPE	0.88	1.11	98.01	[59]

HDPE—high-density polyethylene.

In the literature, in addition to the energetic utilisation of pyrolysis gas, one can find publications on the utilisation of synthesis gas from gasification. Nevertheless, it should be emphasised that gas from gasification has a much lower calorific value (4–15 MJ/m³) compared to pyrolysis gas; hence, its energetic utilisation has a much smaller application potential. An analysis of sources in the literature shows that numerous studies are being undertaken in the world on the utilisation of pyrolysis gas but, to date, no technology has been implemented on a large scale. The methods of utilising pyrolysis gas proposed by researchers are mainly employed on a pilot or laboratory scale.

The problem of managing the environmentally burdensome gaseous products of the thermal conversion of selected calorific wastes is of an applied nature, as evidenced by the interest of both waste and metallurgical entrepreneurs, for reasons including the following:

- The possibility of managing environmentally hazardous plastic waste, RDF waste and post-production bio-waste, as well as the gaseous products of the thermal conversion of these wastes;
- The possibility of reducing the use of natural gas to fuel heating furnaces, which will translate into economic benefits.

Therefore, there is an urgent need to develop this research towards selecting the most effective and economically viable solution.

While pyrolytic gas has been studied as an alternative to fossil fuels in various contexts, the specific application within the iron and steel industry, particularly in heating furnaces, remains significantly underexplored. To our knowledge, no prior research has addressed the use of pyrolytic gas for furnace heating in this sector.

Additionally, our research demonstrates how the co-firing of pyrolytic gas with natural gas can lead to substantial natural gas savings. Even a small fraction of pyrolytic gas in the fuel mixture results in significant reductions in natural gas consumption, given the high energy demands of the heating process in steel production. This leads not only to cost reductions but also to lower carbon emissions and improved energy efficiency.

Thus, the incorporation of pyrolytic gas addresses a key gap in both academic research and industrial practice by highlighting the potential economic and environmental benefits of reducing natural gas dependency in steel production.

This paper is organised as follows. Section 2 discusses the materials and methodology used in the research conducted in this paper. Section 3 presents and discusses the results of computer simulations obtained in the study. Section 4 is a discussion of the results and a summary of all the observed observations.

2. Materials and Methods

The work carried out for the purposes of this article was divided into two stages: experimental preliminary studies, performed in a laboratory chamber, and computer simulations performed using the Ansys Chemkin-Pro computer programme (ver. 2021 R1). The scheme of the conducted research work is shown in Figure 1.

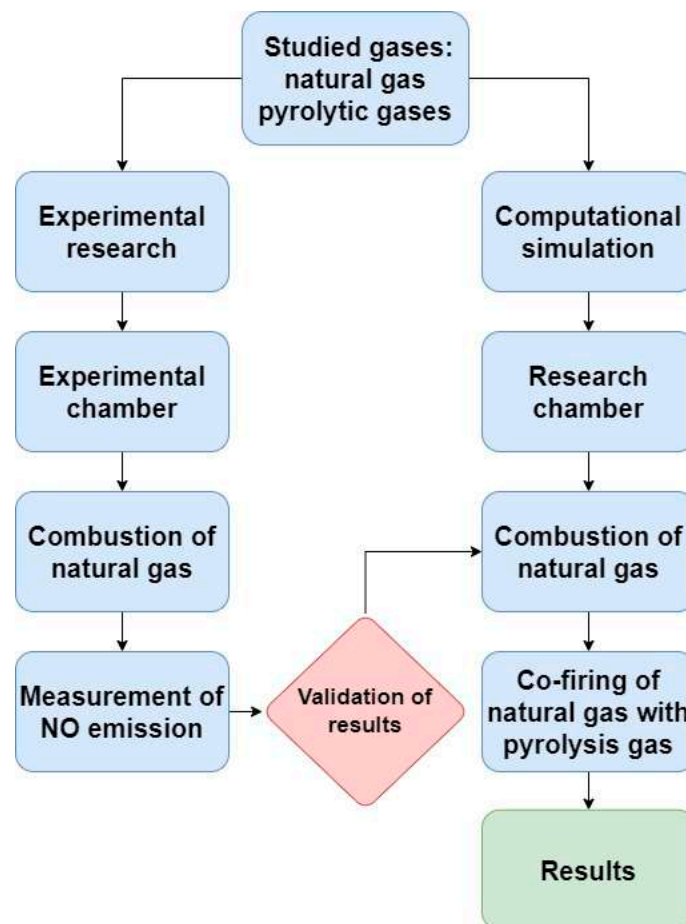


Figure 1. Scheme of conducted research work.

In the first stage, in the experimental part, the scope of the research included determining the temperature profile and concentration of selected pollutants, namely NO, during the combustion of natural gas in the heating chamber. In the second stage, computer simulations were carried out by means of the Ansys Chemkin-Pro programme (ver. 2021 R1), within which the chemical composition of the following products was modelled:

- Natural gas combustion.
- Co-combustion of natural gas with pyrolysis gases from the thermal conversion of various wastes.

The calculations were performed for the heating zone of a pusher furnace for hot forming, located in one of the steelworks in Poland, in the Heavy Plate Rolling Mill. The results obtained from the modelling were verified by comparing the calculated NO concentrations during the combustion of natural gas with the results obtained under experimental conditions.

2.1. Material

Four gases were selected for computer simulations from the thermal conversion of two types of RDF and a mixture of *alder* chips with polypropylene and a mixture of *pine* chips and polypropylene. The main reason for choosing this waste combination is the local circumstances and waste availability. Both *pine* and *alder* waste are sawmill and furniture industry by-products. They can be successfully used for energy purposes. The problem, however, is with polypropylene waste, which is not recyclable due to contamination. The properties of plastics and their high calorific value limit their thermal conversion. RDF in Poland does not have a permanent customer, which means that huge quantities are stored. The mixture of the above-mentioned wastes proposed in the article, among other reasons due to its calorific value, enables them to be thermally converted and the products of this process are suitable for further use. Moreover, the addition of polypropylene waste to *pine* and *alder* waste allows one to minimise the effects of incorrect segregation and managing problematic waste.

2.2. Modelling Procedure in Ansys Chemkin PRO (Ver. 2021 R1)

Computer calculations were carried out using the licenced CHEMKIN-PRO software (ver. 2021 R1). A detailed GRI-Mech 3.0 chemical mechanism developed by the University of California, enriched with C1-C6 hydrocarbons, including kinetic data of more than 60 compounds and nearly 350 chemical reactions, and thermodynamic and transport data, was implemented for the calculations. In addition to the elements and compounds involved in the combustion process, the kinetic data file contained a set of reactions together with values to calculate reaction rate constants from the Arrhenius Equation (1) [65]:

$$k = AT^b \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where

A —pre-exponential multiplier (pre-exponential constant).

b —temperature exponent.

E —activation energy, J/mol.

R —universal gas constant = 8.314 J/(mol K).

T —absolute temperature in the reaction zone, K.

The programme used for modelling is used for the chemical analysis of phenomena and processes occurring during the thermal conversion of fuels and waste, and the model adopted for the calculations does not take into account the phenomenon of diffusion. At the core of the model, there is a chemical mechanism that has been implemented from The Creck Modelling Group. The chemical mechanism is based on the Arrhenius reaction rate constant equation.

For the calculations, a model was used based on the condition of ideal mixing of the reactants, the so-called “Perfectly Stirred Reactor”, and a model with a free-spreading flame reactor, “The Freely Propagating Flame Reactor”. The first model was used for combustion calculations in the burner, while the second model was used in the test chamber. Based on the results from the preliminary tests carried out in the laboratory chamber, the necessary data were obtained to formulate the boundary conditions in the modelling procedure. The obtained results provided information concerning temperature distribution and flow parameters, such as pressure and amount of media fed.

Selecting the reactor was also based on the experience of other researchers who have successfully used this type of reactor for modelling thermal conversion processes of solid fuels and waste. It is noteworthy, as pointed out in their paper by Che et al. [66], that great advances in the numerical simulation of thermal conversion technology for solid fuels and waste have been made by the Huazhong University of Science and Technology State Key Laboratory of Coal Combustion. They used the HSC chemistry package and the PSR model to simulate the thermodynamic equilibrium and dynamic equilibrium of the palm oil waste pyrolysis process, obtaining very good conformity with the experimental results.

The chemical mechanism adopted for the calculations has been repeatedly used by Ranzi, Faravelli and Frassoldati [67–70], as well as by the authors of this paper, to model the chemical kinetics of combustion, pyrolysis and gasification of various biomass species. It is noteworthy that the mechanism was validated with the results obtained from the experiments, which increases the reliability of the results obtained from the calculations. For the calculations, the assumption was made that combustion takes place in a reactor with perfect mixing of the reactants, i.e., a Perfectly Stirred Reactor (PSR). A model of the conducted calculations is shown in Figure 3.

2.3. Preliminary Research

The preliminary tests were carried out on the experimental stand presented in Figure 2. The main element of the test stand was a high-temperature, cylindrical heating chamber (1), with a diameter of 0.12 m and a length of 3 m, made of a ceramic pipe. In order to reduce heat losses, thermal insulation made of fibrous materials (2) was made along the entire length of the chamber. A 15 kW gas swirl burner (5) was located at the inlet to the chamber. Seven holes (3) were placed along the entire length of the chamber (Table 5), used to measure temperature by means of a PtRh10-Pt thermocouple (6) and the composition of flue gases employing a VARIO PLUS analyser (7). The gas and air volume flow was regulated utilising valves with rotameters (4). Air was supplied from a compressor and natural gas from the grid.

Table 5. Locations of measurement points.

Measurement Point Number	T1	T2	T3	T4	T5	T6	T7
Distance from burner outlet (m)	0.29	0.65	0.97	1.42	1.91	2.51	2.91

The locations of the measurement points are presented in Table 5.

Temperature measurements at individual points along the length of the heating chamber were taken using a 0.5 mm thick PtRh10-t jacketed thermocouple, covered in quartz tubing, placed perpendicular to the flame axis. A BRYMEN 805 digital multimeter was used to read the temperature. The investigations were carried out for the excess air ratio $\lambda = 1.05$. The gas and air flows were kept constant and amounted to, for air, $\dot{V}_A = 0.00428 \text{ m}^3/\text{s}$ and, for gas, $\dot{V}_{NG} = 0.00045 \text{ m}^3/\text{s}$.

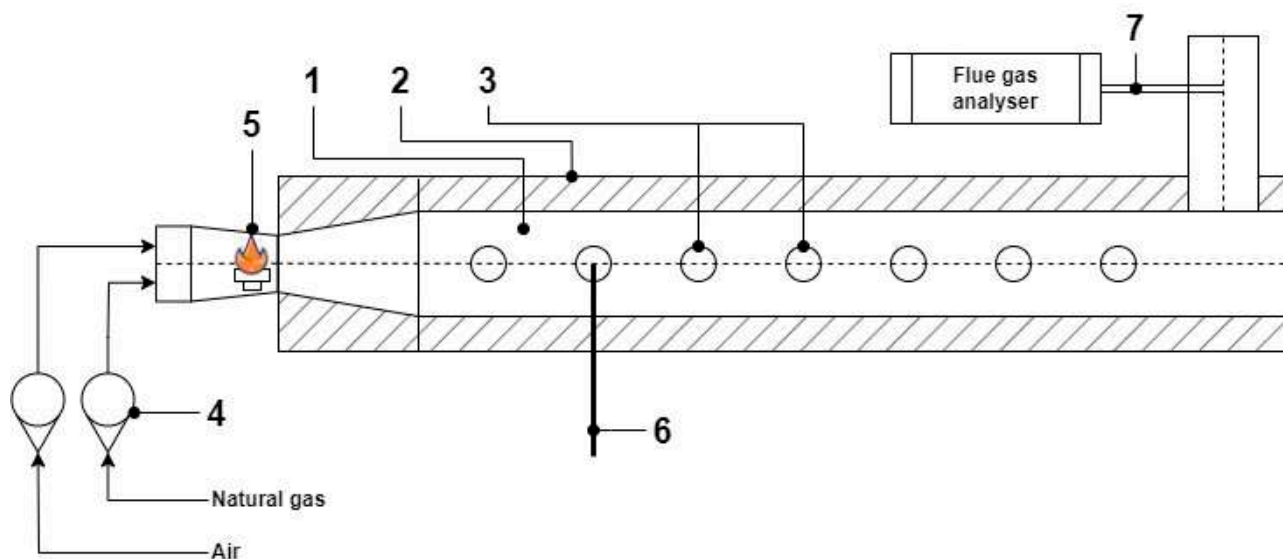


Figure 2. Diagram of experimental station.

2.4. Computer Simulations

Computer simulations were performed using ANSYS Chemkin-Pro software (ver. 2021 R1), version 2021R1 (licence within the Pioneer network). According to the literature data, this is one of the most commonly employed programmes, next to ASPEN PLUS, for modelling chemical phenomena [71–74]. Based on the experience of other researchers [75–79], a modified chemical mechanism was implemented for the calculations, taking into account C1–C5 hydrocarbons, including 360 reactions as well as 61 compounds and chemical elements, with kinetic and thermodynamic data. Two types of reactors were adopted in the modelling procedure. The first, a Perfectly Stirred Reactor (PSR), was the equivalent of gas combustion in a burner, and a plug flow reactor (PFR) had the gas combustion process take place in a heating chamber with a constant temperature profile (Figure 3).

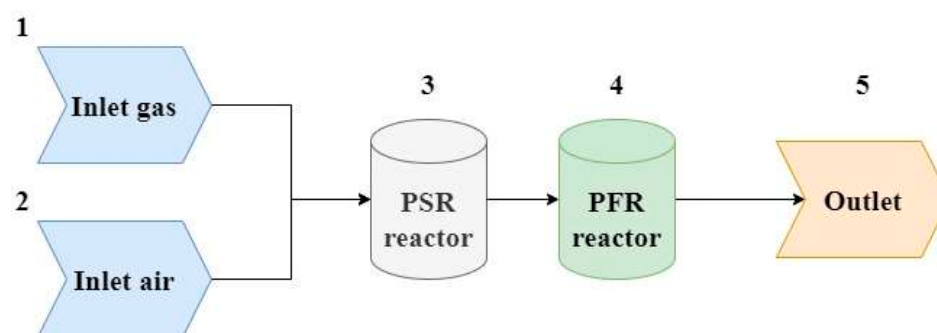


Figure 3. Schematic diagram of applied computational model, where 1—inlet gas; 2—inlet air; 3—PSR; 4—PFR; 5—outlet.

The input data file also included experimentally determined values (Table 6), namely the following:

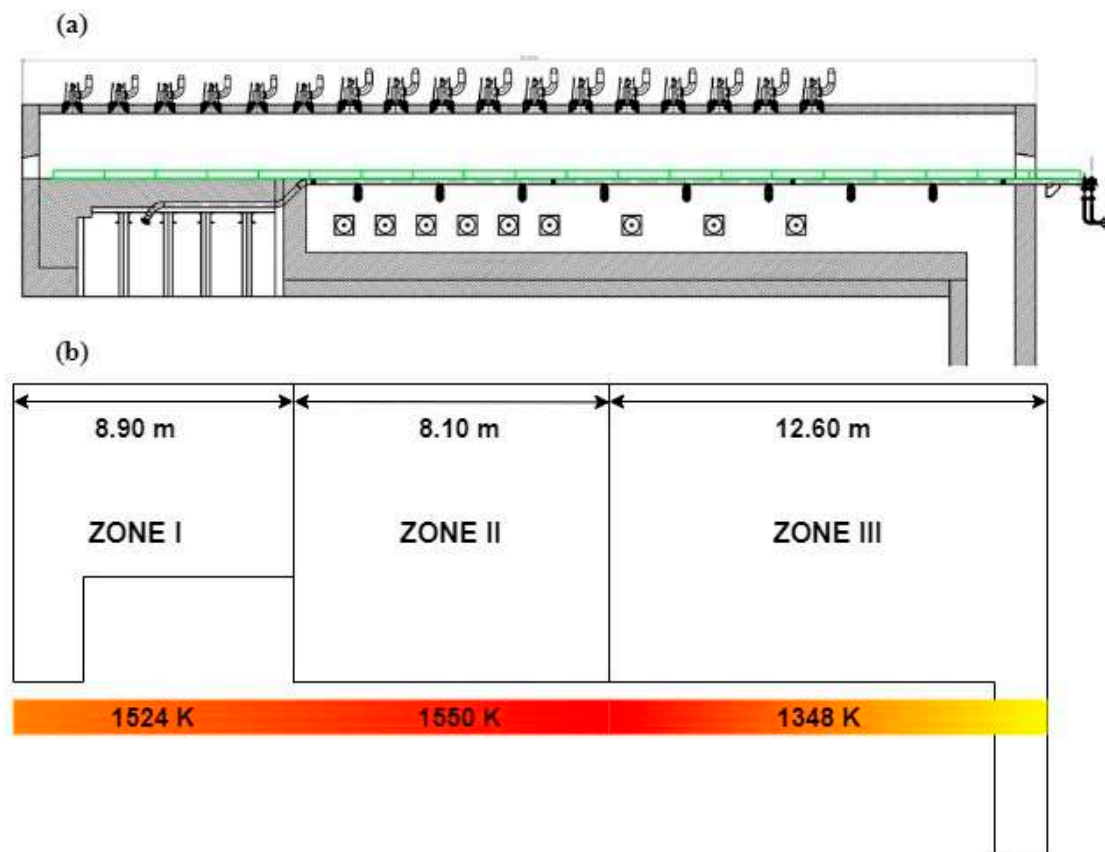
- Mass flow of reactants (air and gas).
- Chemical composition of reagents.
- Temperature of supplied media.
- Pressure.
- Adiabatic combustion temperature.
- Temperature profile in the combustion chamber.
- Chamber dimensions (diameter, length).
- Residence time of the reagents in the highest temperature zone.

Table 6. Input data in modelling procedure for experimental chamber.

Parameter	Value **
Air flow (m ³ /s)	0.00428
Gas flow (m ³ /s)	0.00045
Air temperature (K)	293
Gas temperature (K)	293
Adiabatic temperature * (K)	1980
Chamber length (m)	3
Chamber diameter (m)	0.12
Residence time (ms)	0.15
Pressure (atm)	1

* Adiabatic temperature was calculated for natural gas using Chemkin-Pro software (ver. 2021 R1), Equilibrio model; ** modelling input data taken from the experimental study.

Basic computer simulations were performed for the heating zone of a pusher furnace (Figure 4).

**Figure 4.** Diagram of pusher furnace (a); division of furnace into zones (b) [80,81].

The following gases from waste pyrolysis were analysed:

- RDF (P1, P2) [25,44].
- a mixture of *alder* chips with polypropylene (P3) [82].
- a mixture of *pine* chips with polypropylene (P4) [82].

The streams of the analysed gases ($\dot{V}_{PG}$) were calculated from Relationship (2), using the conversion factor of natural gas to another combustible gas (3):

$$\dot{V}_{PG} = \dot{V}_{NG} \times n \quad (2)$$

$$n = \frac{LHV_{NG}}{LHV_{PG}} \quad (3)$$

where

LHV_{NG} —calorific value of natural gas, MJ/m³.

LHV_{PG} —calorific value of pyrolysis gas, MJ/m³.

The calculated flow rates of the analysed gases and their chemical composition are presented in Table 7, while the remaining parameters utilised in the calculations for the reheating furnace are presented in Table 8. The mixed gas was burned at a ratio of 1:10 to natural gas.

Table 7. Flow rates and chemical composition of analysed gases.

Gas	Natural Gas—NG	RDF ₁ —P1	RDF ₂ —P2	AW + PP * —P3	PW + PP * —P4
LHV (MJ/m ³)	34.4	29.94	24.2	21.67	24.2
n	1	1.145	1.410	1.587	1.421
$\dot{V}_{NG}$ (m ³ /s)	0.3669	0.3302	0.3302	0.3302	0.3302
$\dot{V}_{PG}$ (m ³ /s)	-	0.0420	0.0517	0.0582	0.0521
Gas composition (vol%)					
H ₂	-	12.37	13.2	8.28	7.94
CO ₂	0.315	11.89	21.1	32.65	29.44
CO	-	29.69	19.8	27.07	26.43
CH ₄	96.648	17.83	18.9	16.47	23.15
C ₂ H ₄	-	13.84	7.1	1.6	1.47
C ₂ H ₆	1.836	4.03	2.3	3.08	2.88
C ₃ H ₆	-	7.34	-	5.34	5.56
C ₃ H ₈	-	0.43	6.1	1.15	1.08
C ₄ H ₁₀	-	0.05	3.7	0.41	0.47
C ₅ H ₁₂	-	0.01	-	1.41	0.28
N ₂	1.201	-	-	-	-
Ref.	[83]	[44]	[25]	[82]	[82]

* Ratio in both mixtures was 70% wood chips and 30% polypropylene.

Table 8. Input data in modelling procedure for reheating furnace.

Parameter	Value *
Air temperature (K)	623
Gas temperature (K)	293
Combustion chamber temperature (K)	1550
Chamber length (m)	8.1
Cross section (m ²)	9.75
Residence time (ms)	1
Pressure (atm)	1
Air flow $\dot{V}_{Air}$ (m ³ /s)	35.583

* Input data for modelling was provided by the local steelworks.

3. Results

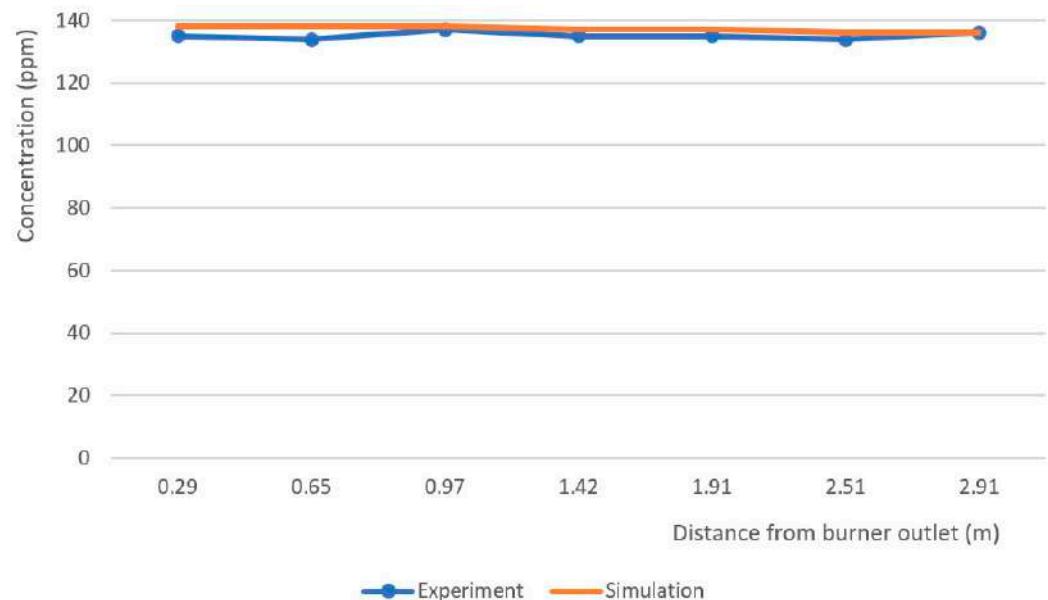
3.1. Combustion of Natural Gas in a Laboratory Chamber

The measured values of NO concentration and temperature in the laboratory chamber are summarised in Table 9.

The experimentally determined temperature profile (Table 9) was implemented in computer simulations and then the results for the NO concentration obtained from the calculations and the experiment in the laboratory chamber were compared (Figure 5).

Table 9. Temperature and NO concentration distribution along length of experimental chamber.

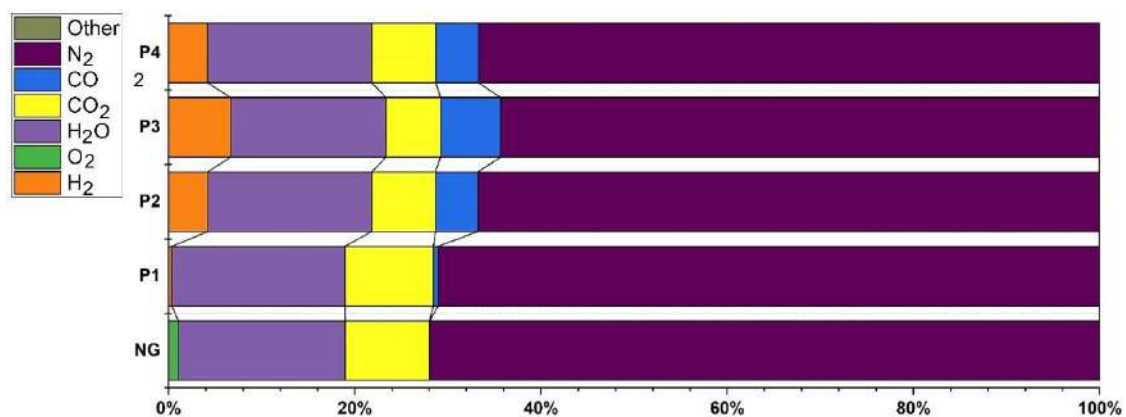
Distance from Burner Outlet (m)	0.29	0.65	0.97	1.42	1.91	2.51	2.91	Measurement Uncertainty
NO Concentration (ppm)	135	134	137	135	135	134	136	± 5 ppm
Temperature (K)	1583	1488	1413	1302	1194	1101	996	± 1 °C

**Figure 5.** Molar concentration of NO as a function of distance from burner.

As can be seen, the obtained simulation results are very similar to the results obtained in the laboratory experiment, which allows us to assume that the model adopted for calculations correctly reflects the conditions prevailing during the combustion of natural gas in the chamber. The above statement was the basis for conducting the simulation of the co-combustion process of natural gas with gases from waste pyrolysis in a metallurgical reheating furnace.

3.2. Co-Combustion of Gases from Waste Pyrolysis in Reheating Furnace

Calculations were performed both for the co-combustion of the pyrolysis gases listed in Table 9 with natural gas and for natural gas alone. The results obtained for the main combustion products at the end of the heating zone are presented in Figure 6, while Figures 7 and 8 additionally show the change in the concentration of NO, CO, CO₂, H₂ and unburned hydrocarbons as a function of the zone length.

**Figure 6.** Molar concentration of main combustion products and co-combustion of natural gas with waste pyrolysis gases at end of heating zone (8.1 m).

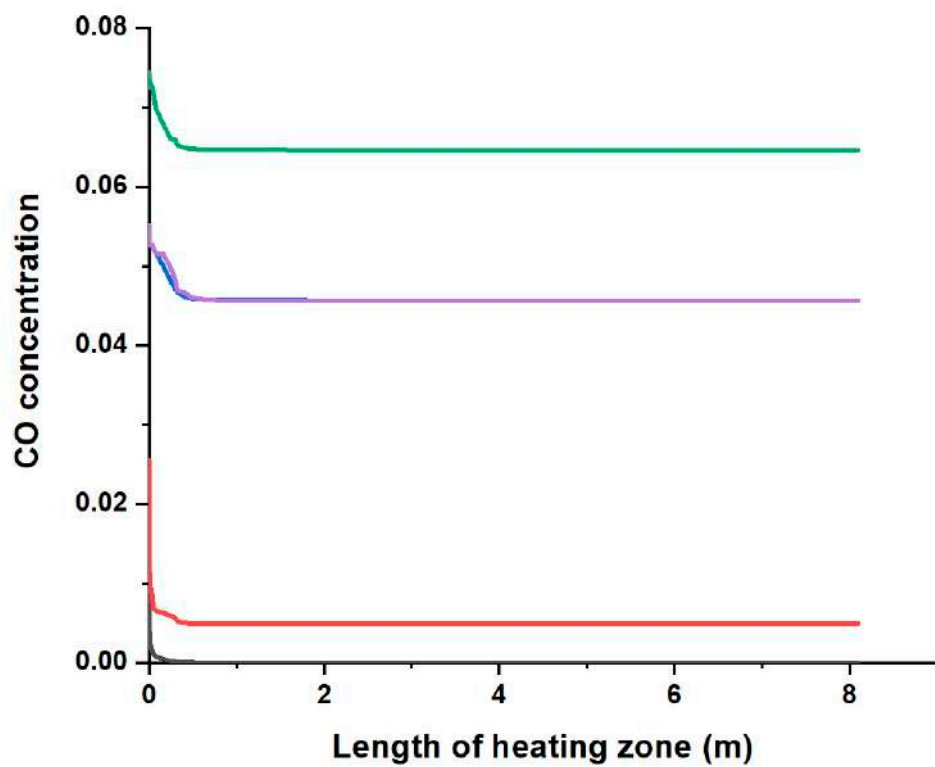
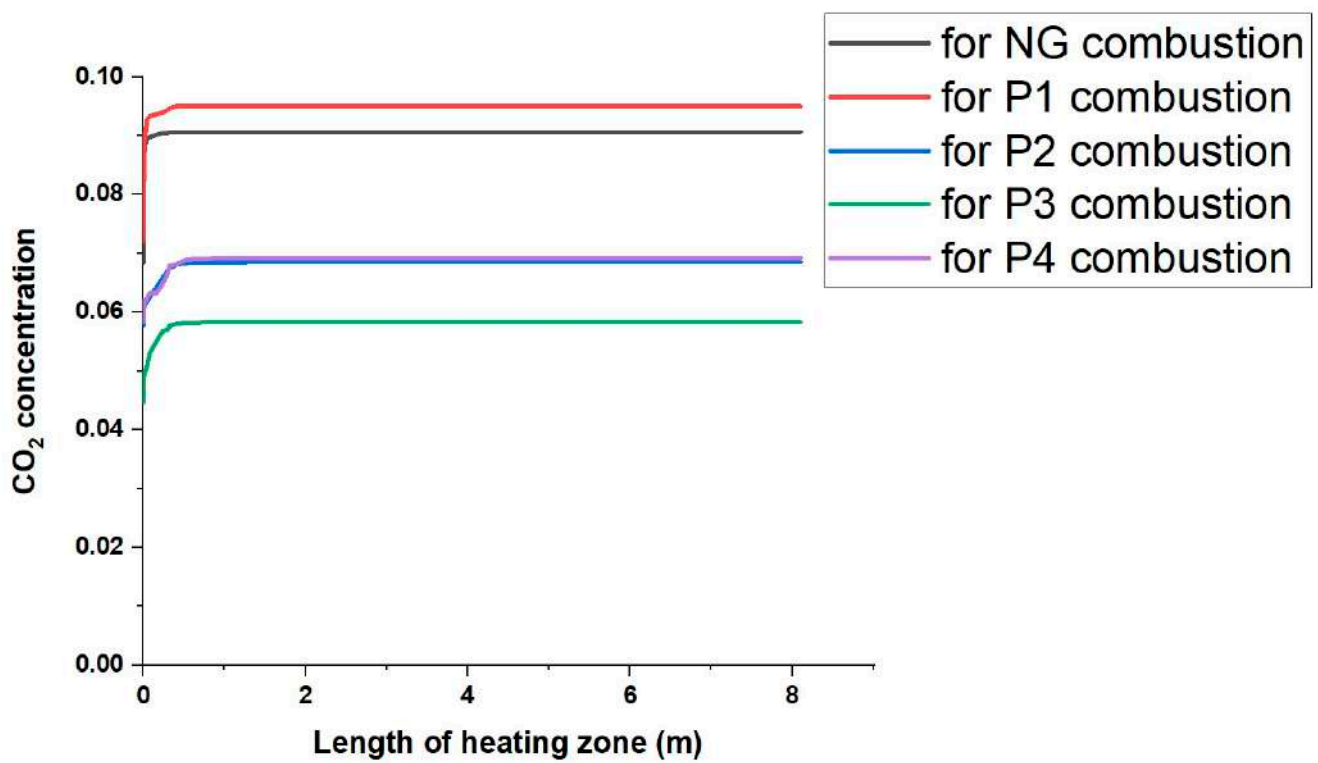


Figure 7. Cont.

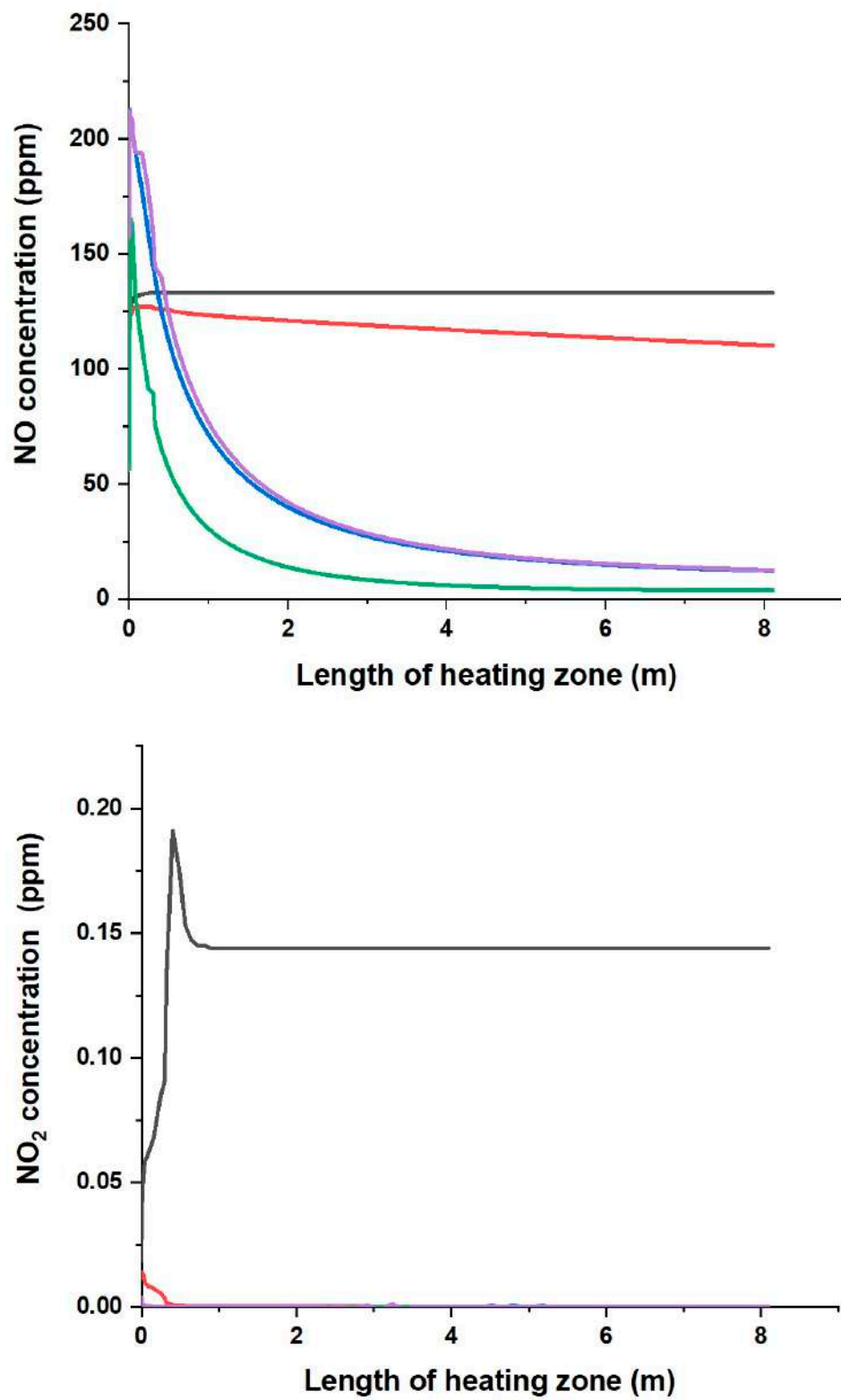


Figure 7. Cont.

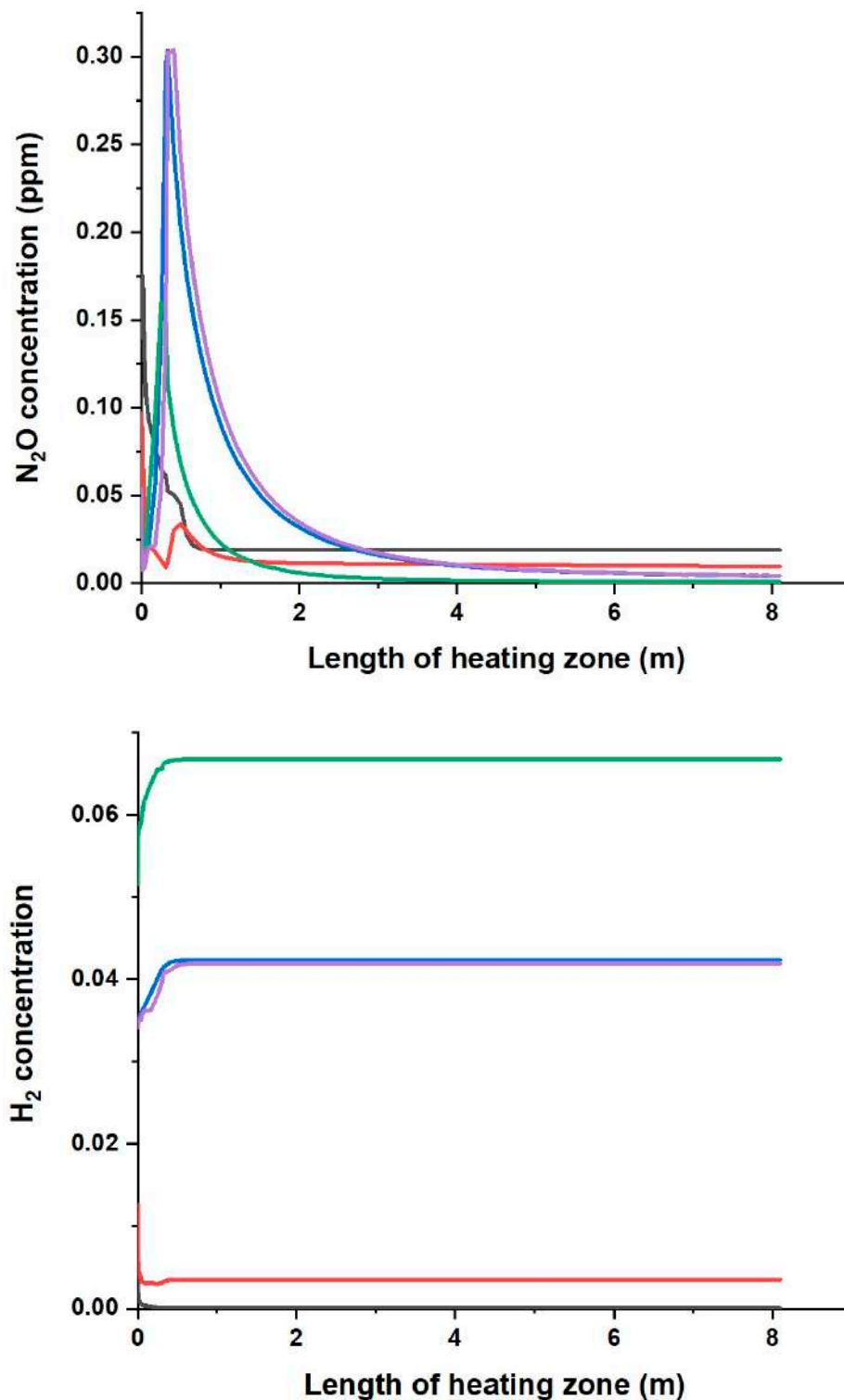


Figure 7. Concentration of selected pyrolysis gas products as function of heating zone length.

The performed computer simulations (Figures 6 and 7 show that the chemical composition of the flue gases from the co-combustion of pyrolysis gases is qualitatively similar to the composition of the flue gases obtained from the combustion of natural gas alone. Quantitatively, however, differences are observed for the CO and H₂ concentrations, which are related to the composition of the pyrolysis gas. The smaller the share of CO and H₂ in the composition of the pyrolysis gas, the lower the concentration of these compounds is in the combustion products. The highest concentration of CO and H₂ in the flue gases was

observed for the co-combustion of natural gas with gas from the pyrolysis of *alder* chips with polypropylene (P3) and amounted to 6.67% for H₂ and 6.46% for CO, respectively. The lowest concentrations were recorded for the gas from the pyrolysis of RDF (P1) and amounted to 0.35% for H₂ and 0.49% for CO, respectively. The fraction of polypropylene in the P3 and P4 mixtures was 30%.

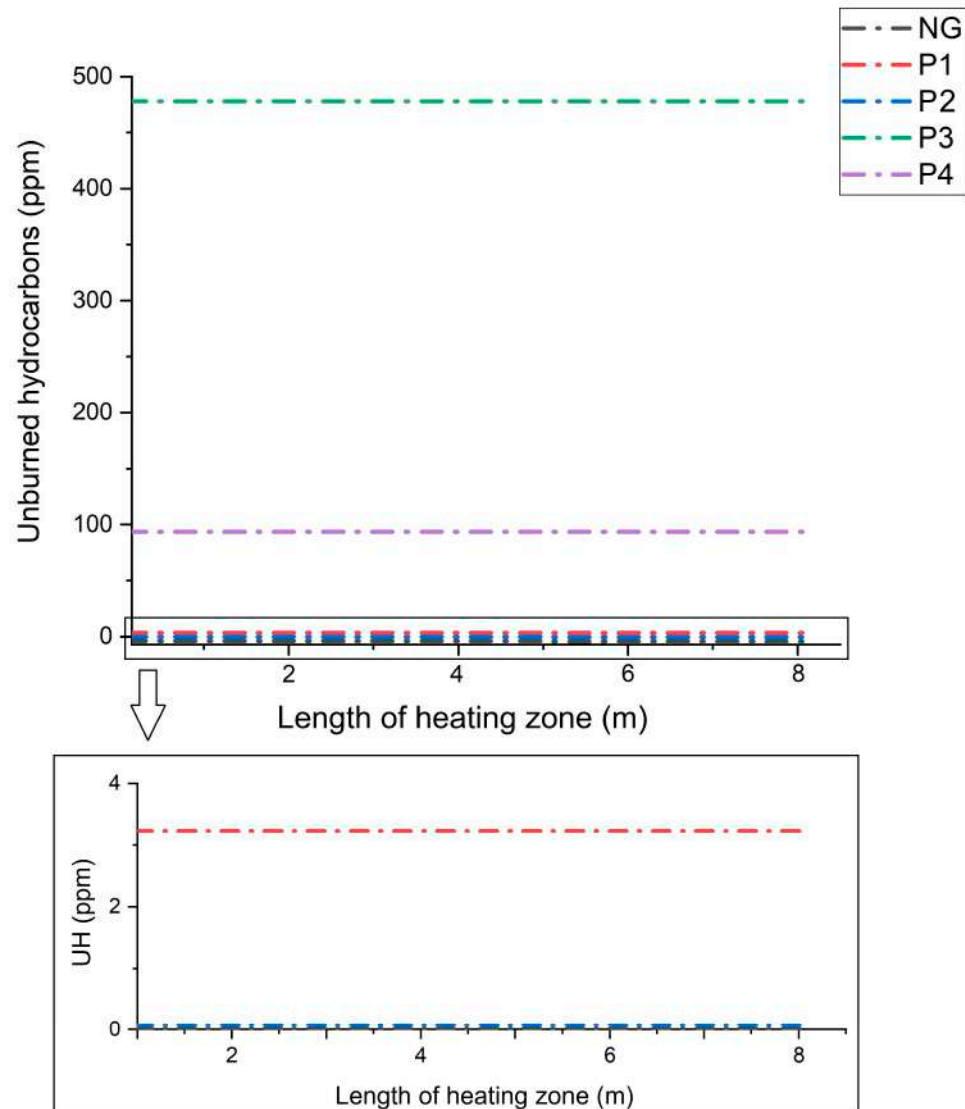


Figure 8. Concentration of unburned hydrocarbons as a function of heating zone length.

The concentrations of the analysed compounds, both from the combustion of natural gas alone and from co-combustion with pyrolysis gases along the length of the heating zone, have a linear course for most of them, namely CO, CO₂ and H₂. A different situation is observed for nitrogen oxides: NO, NO₂ and nitrous oxide, N₂O. The highest concentrations occur in the burner zone, and then they drop rapidly, which is related to the high temperature in the PSR, responsible for the formation of the so-called thermal nitrogen oxides. For all the analysed variants, the lowest NO concentration is observed for the P3 gas and it is 12 ppm, while the highest is for natural gas alone and it is 133 ppm. The highest NO₂ concentration is for natural gas and it is 14 ppm; the lowest is for the P3 gas—0.03 ppm. The N₂O concentration is also the highest for natural gas and it is 0.02 ppm, whereas the lowest concentration reaches 0.001 ppm for the P3 gas. In combustion products, in addition to a significant share of compounds such as H₂, O₂, H₂O, CO₂, CO and N₂, there are also compounds whose share is trace, included in Figure 10 in the “other” category. These include, among others, the above-mentioned NO, NO₂ and N₂O. The concentration of

other compounds is the highest for the P3 gas and is 0.07%, while the lowest is for NG and P4—0.02%.

As for the concentration of unburned hydrocarbons (Figure 8), the highest values are observed during the combustion of P3 gas and amount to about 500 ppm. Such a high value may result from the higher concentration of C5 hydrocarbons in the fuel mixture compared to the other combusted mixtures. On the other hand, the lowest trace concentration was observed during the combustion of NG and mixtures with the P1 and P2 gases. From the technological point of view, unburned hydrocarbons and CO and H₂ formed during the combustion of mixtures with natural gas will burn out in the furnace equalisation zone due to the excess air ratio prevailing there ($\lambda = 1.07$).

In order to explain the mechanisms responsible for the formation of the analysed compounds, a formation pathway analysis and sensitivity analysis were performed in the Ansys Chemkin-Pro programme (ver. 2021 R1).

3.3. Measurement Error Analysis

The analysis of measurement errors introduced in the course of experimental tests includes systematic errors, resulting from the design of the measurement apparatus, as well as the measurement methodology. The measurement of nitric oxide concentration carried out with the Testo 360 analyser is subject to an error, the magnitude of which depends on its accuracy class [84,85]:

$$kl = \frac{\Delta x_{max}}{Z} \cdot 100\% \quad (4)$$

From the given instrument class, the absolute error value can be calculated:

$$\Delta x_{max} = \frac{kl \cdot Z}{100} \quad (5)$$

The accuracy of the exhaust gas analyser, for the final value of the measuring range, i.e., 200 ppm, according to the verification certificate, was 3.8%.

The actual temperature t at each point of the flame was calculated according to Formula (6) derived from the weld energy balance [84]:

$$t = t_s = a \cdot \varepsilon_s \cdot C_c \cdot d_s \left[\left(\frac{T_s}{100} \right)^4 - \left(\frac{T_w}{100} \right)^4 \right] \quad (6)$$

where

t_s, T_s —weld temperature, °C; K.

$a = 5$ —experimental constant, m·K/W.

$C_c = 5.67$ —blackbody radiation constant (Stefan Boltzman constant), W/m²·K.

d_s —thermocouple weld diameter, m.

ε_s —emissivity of the thermocouple weld; for the PtRh-Pt thermocouple used in the measurements $\varepsilon_s = 0.000106 t_s + 0.0383$.

$T_w = 293$ —ambient temperature, K.

The maximum temperature difference between the measured and calculated temperatures was 13 °C.

The maximum concentration difference between the measured and calculated value with respect to the standard oxygen concentration was 20 ppm, and the minimum was 2.5 ppm. The characteristics of parameters for the used measuring devices are shown in Table 10.

Table 10. Characteristics of measurement parameters.

Measured Quantity	Measurement Range	Accuracy	Resolution
VARIO PLUS analyser			
NO, ppm	0 ÷ 5000	±5 ppmv ±5% (<1000 ppmv) ±10% (>1000 ppmv)	1.00
PtRh10-Pt thermocouple			
Temperature, °C	Up to 1800	±1	0.10

3.4. Formation Path Analysis and Sensitivity Analysis

As mentioned earlier, owing to the complexity of the kinetics of chemical reactions occurring during the co-combustion of pyrolysis gases, the NO formation paths (Figure 9) and reactions involved in the formation of compounds such as NO, NO₂, N₂O, CO, CO₂ and H₂ were analysed. Sensitivity analyses were also performed for all the studied gas mixtures. The results of the analyses are presented in Figures 10–12.

By analysing the formation paths, it can be seen that the mechanism of nitrogen oxide formation during the combustion of mixtures of natural gas with the P2, P3 and P4 gases is much more complex than that for the combustion of natural gas alone and with the P1 gas. The NO formation pathway is the same for NG and P1, but differences are observed in the rate values, as presented in Figure 10a,b. In NO formation, not only CH radicals participate, but also HNO, NCO, NH, HCN, NH₂, HNCO and H₂O. In order to explain the reason for the observed differences, a sensitivity analysis was performed (Figure 10) [86].

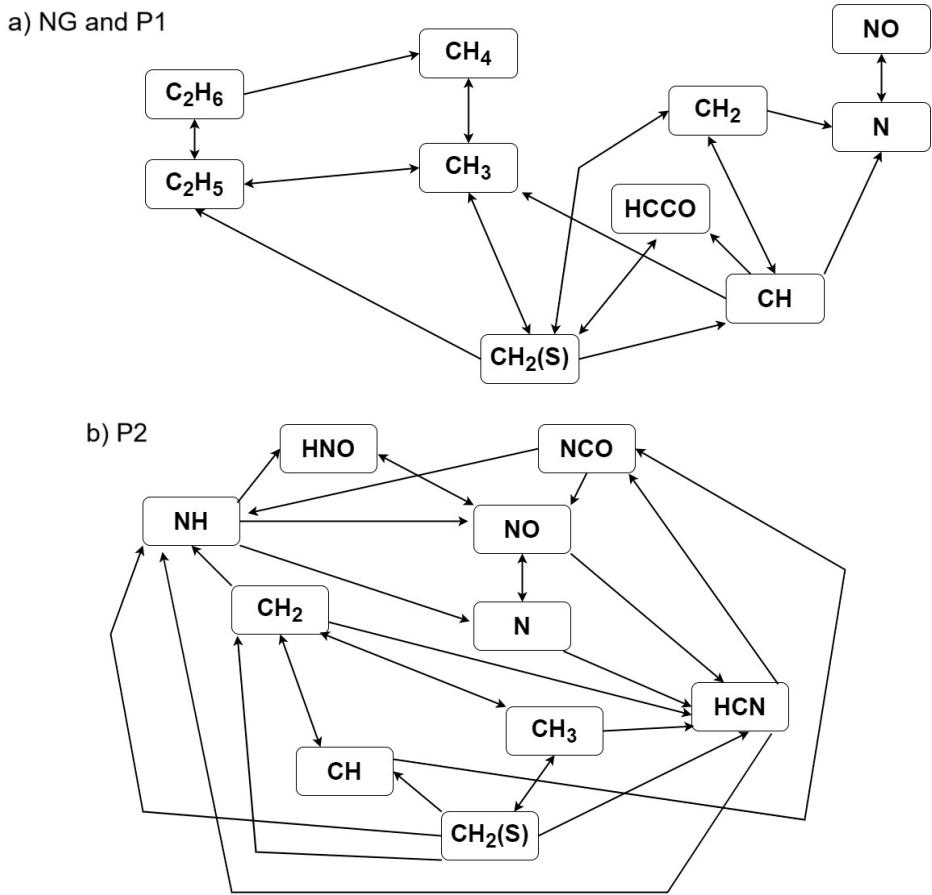


Figure 9. Cont.

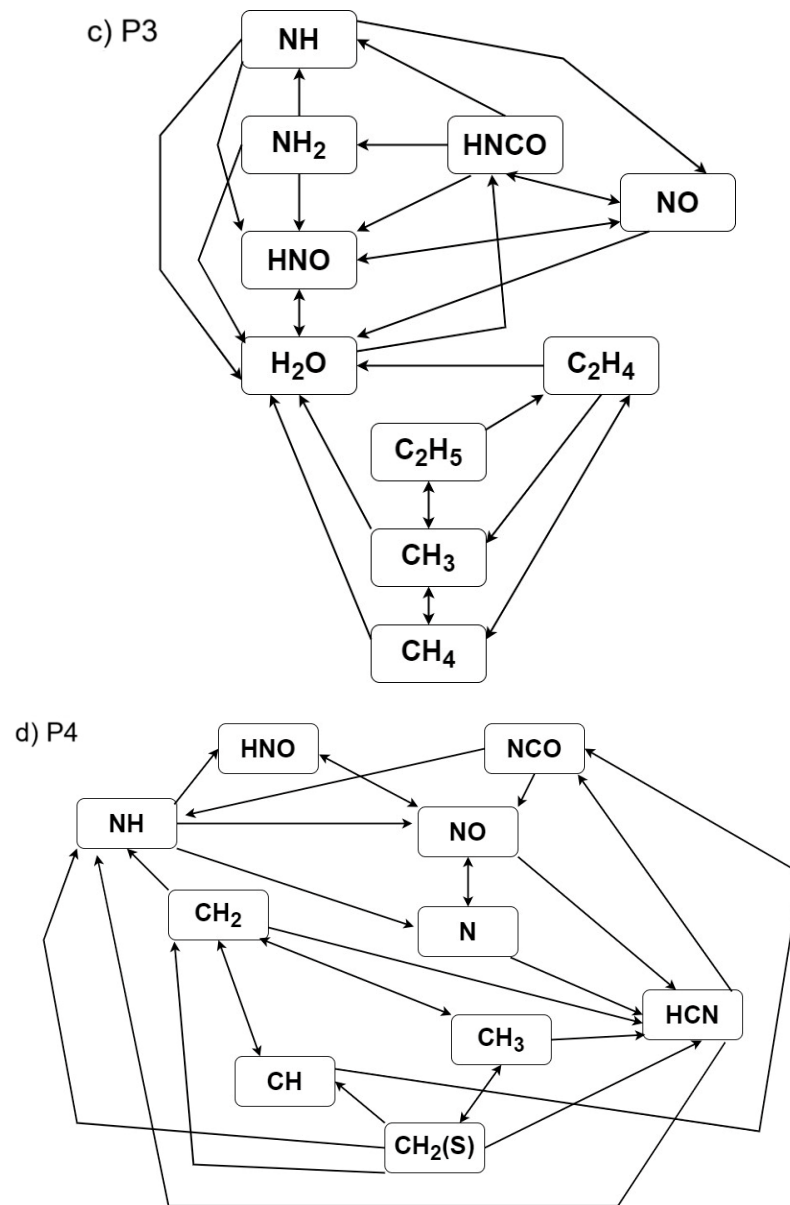


Figure 9. NO formation paths.

The dominant reactions responsible for the formation of NO (Figure 10) during the combustion of natural gas are Reactions (7)–(9):



the reactions that are mainly responsible for the decomposition of NO are Reactions (10) and (11):



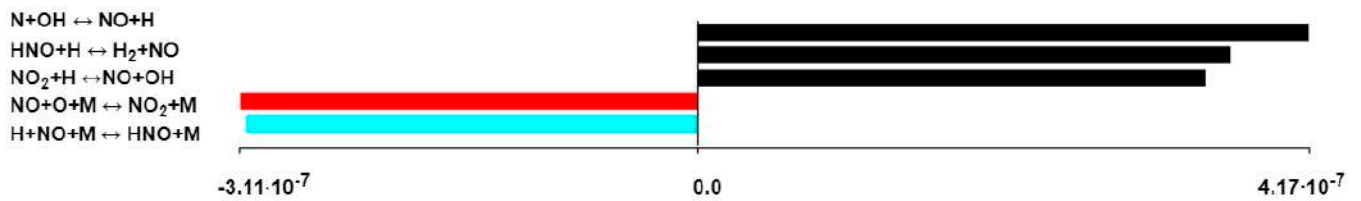
During the combustion of gas mixtures P1, P2 and P4, Reactions (7) and (8) are also dominant. In the case of the combustion of gas mixture P3, the main reaction of NO formation is Reaction (8), which has the largest share of NO formation for this mixture. The most important reactions responsible for NO decomposition during the combustion of gas

mixture P1 are also Reactions (11) and (10), just as in the case of natural gas. During the combustion of mixture P2, the reactions responsible for NO decomposition are (12), (13) and (14):

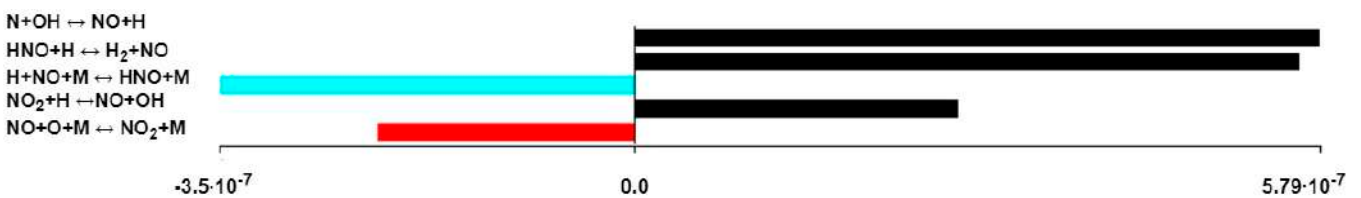


(a) NG

H ■ O ■ OH ■ HO₂ ■



(b) P1



(c) P2



(d) P3

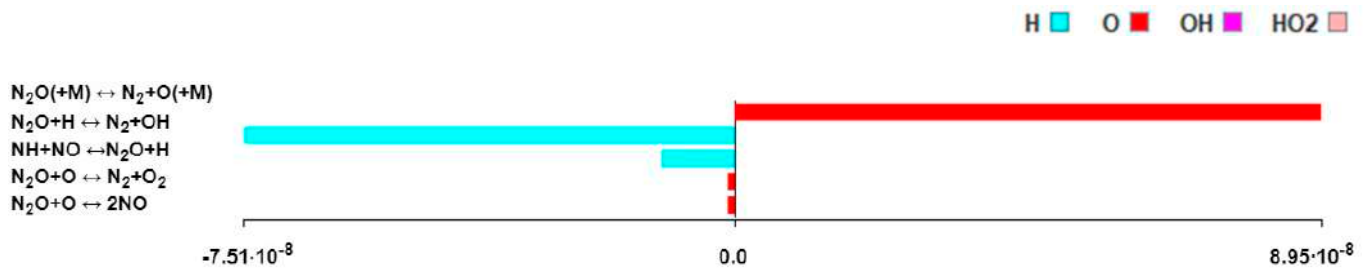


(e) P4

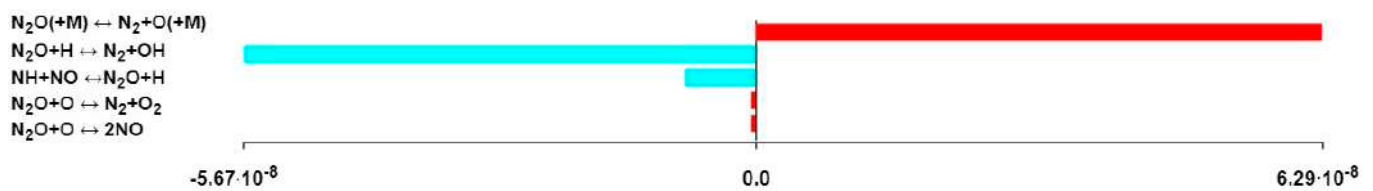


Figure 10. NO formation rate for set of reactions implemented for calculations.

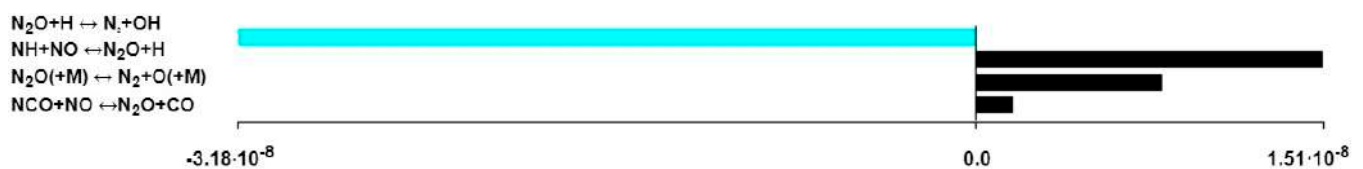
(a) NG



(b) P1



(c) P2



(d) P3



(e) P4



Figure 11. N_2O formation rate for set of reactions implemented for calculations.

For the P3 mixture, this is only Reaction (15):



And for the P4 mixture, Reactions (12)–(14) are exactly the same as for the P2 mixture.

By analysing the rate of N_2O formation (Figure 11) for all the considered variants, it can be seen that the dominant N_2O formation reaction for NG and P1 is Reaction (16):



(a) NG

H ■ O ■ OH ■ HO2 ■

(b) P1



(c) P2



(d) P3



(e) P4



Figure 12. NO_2 formation rate for set of reactions implemented in calculations.

For mixtures P2, P3 and P4, there are three main reactions: (16)–(18).



In turn, the dominant reaction responsible for the decomposition of N_2O in the case of all the combusted gases and mixtures is Reaction (19):



By observing the NO₂ formation rate (Figure 12) for all the considered variants, it can be seen that the dominant NO₂ formation reactions for all the combusted fuels are Reactions (20) and (21):



On the other hand, NO₂ decomposition is most influenced by Reaction (22), which is responsible for NO₂ decomposition during the combustion of all the gases:



Formation pathways with interpretations of the results for compounds such as CO, CO₂ and H₂ can be found in the Supplementary Materials to complement the above analysis.

As can be seen in Figures 10–12, the rate of formation of the selected compounds for the same reactions varies depending on the fuel composition. Temperature does not affect the rate of formation of compounds in this case because it is constant along the entire length of the heating chamber (1550 K).

4. Conclusions

The issue of managing the environmentally harmful gaseous products of the thermal conversion of selected calorific wastes discussed in this article addresses the problems faced by both the waste industry and highly energy-intensive industries, such as the steel industry. The results presented in this paper clearly indicate that it is possible to safely manage environmentally harmful gaseous products from the pyrolysis process of selected wastes for firing metallurgical reheating furnaces, both in terms of technology and the environment. The detailed analysis of the chemical mechanisms describing the process of the co-combustion of pyrolysis gases with natural gas in the heating zone of the pusher furnace provides comprehensive knowledge on combustion kinetics and environmental effects, namely the following:

- The performed computer simulations show that the chemical composition of the flue gases resulting from the co-combustion of pyrolysis gases is qualitatively similar to the composition of flue gases obtained from the combustion of natural gas alone.
- The results most similar to the combustion of natural gas alone, in terms of the composition of the flue gases, were obtained for the P1 mixture.
- The greatest influence on the differences in the composition of the resulting flue gases is the composition of the pyrolysis gas co-fired with natural gas.
- The addition of gas from the pyrolysis of biomass waste with the addition of PP leads to a higher concentration of CO and H₂ as well as unburned hydrocarbons in the flue gases than for the other mixtures.
- The smaller the share of CO and H₂ in the composition of the pyrolysis gas, the lower the concentration of these compounds in the combustion products is.
- The highest concentration of CO and H₂ in the flue gases was observed for the co-combustion of natural gas with gas from the pyrolysis of *alder* chips with polypropylene (P3), while the lowest was for the gas from the pyrolysis of RDF (P1), which is related to the addition of polypropylene in the P3 and P4 mixtures at a level of 30%.
- By analysing the formation paths, it can be seen that the mechanism of nitrogen oxide formation during the combustion of mixtures of natural gas with the P2, P3 and P4 gases is much more complex than for the combustion of natural gas alone and with P1 gas. In NO formation, not only do CH radicals participate, but so do HNO, NCO, NH, HCN, NH₂, HNCO and H₂O.

The study also showed a number of environmental benefits:

- The analysis has shown that the addition of pyrolysis gas does not increase nitrogen oxide emissions, which will not result in increased emission charges.

- Managing unused waste, including agricultural waste, will have a positive impact on the waste market in Poland. Large companies (e.g., steel mills) using pyrolysis to meet their own energy needs will become regular consumers of this waste.
- We will see the formation of an outlet market for RDF waste, which, in Poland, due to legal conditions, is stored without thermal use.

We will see the dissemination of new solutions concerning thermal waste treatment technologies into the existing waste management system. In conclusion, it should be emphasised that knowledge of the chemical mechanisms presented in the article, in the application context, may enable appropriate actions to be taken aimed at managing gases after the thermal conversion of waste, while maintaining correct operation of the heating chamber and minimising pollution. By analysing the obtained results, it can be clearly stated that the most desirable gases, potentially used for co-combustion in the steel industry, will be gases from RDF pyrolysis because the obtained flue gases are very similar in composition to the flue gases from pure natural gas, which will not translate into an increase in emission fees, and will contribute to a significant reduction in the operating costs of individual furnaces in the steel industry. This study constitutes an introduction into further simulations and pilot-scale studies to confirm the feasibility of effectively replacing natural gas with other alternative fuels. The complexity of the pyrolysis process, making it difficult to describe mathematically, is undoubtedly a disadvantage. However, the selection of boundary conditions and laboratory tests will be able to validate the validity of the computational model and narrow down the parameters that should be used at the laboratory and pilot scales. Moreover, the focus should be on selecting process parameters so that no additional costs are incurred due to excess air emissions.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr12122728/s1>. Figure S1. CO formation rate for set of reactions implemented in calculations. Figure S2. CO₂ formation rate for set of reactions implemented in calculations. Figure S3. H₂ formation rate for the set of reactions implemented in the calculations.

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Economic benefits for the metallurgical industry from co-combusting pyrolysis gas from waste

Magdalena Skrzyniarz^a, Marcin Sajdak^b, Anna Biniek-Poskart^c, Andrzej Skibiński^c,
Artur Maroszek^d, Paweł Niegodajew^e, Monika Zajemska^{a,*}

^a Czestochowa University of Technology, Faculty of Production Engineering and Materials Technology, Armii Krajowej 21, 42-200, Czestochowa, Poland

^b Silesian University of Technology Faculty of Energy and Environmental Engineering, Department of Air Protection, Stanisława Konarskiego 18, 44-100, Gliwice, Poland

^c Czestochowa University of Technology, Faculty of Management, Armii Krajowej 21, 42-200, Czestochowa, Poland

^d Iron Foundry in Myszków, CEMA-MYSTAL, Metalurgiczna 5, 42-300, Myszków, Poland

^e Czestochowa University of Technology, Department of Thermal Machinery, Armii Krajowej 21, 42-200, Czestochowa, Poland

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ABSTRACT

The paper presents some benefits that can be gained in the metallurgical industry from utilizing pyrolysis gas obtained from biomass and plastic waste, in particular in a pusher type reheating furnace. The typical fuel composition that normally involves a mixture of natural gas and coke oven gas was modified by introducing a 9–16 % share of pyrolysis gas. The materials used in the production of the pyrolysis gas were alder and pine chips, as well as polypropylene waste. For all these materials, the contents of carbon, hydrogen, nitrogen, sulfur and oxygen were experimentally estimated on a test stand for solid fuel conversion in a stationary bed at the temperature of 600 °C. The design capacity of the furnace was 90 t/h and the installed power of the furnace was 72.3 MW. Based on data gained from the rolling mill of a steel mill located in Poland, analysis of the profitability of using pyrolysis gas for co-combustion with coke oven gas and natural gas in an industrial heating furnace was carried out. As a result, a significant benefit can be achieved, namely reduced production costs of the analyzed steel company by utilizing pyrolysis gas, leading to an increase in the attractiveness of the plant's products. Plastic waste and biomass are employed as energy sources in the suggested technology, therefore using them as feedstock for the pyrolysis reactor combined with the pusher type metallurgical reheating furnace is a potential proposal for the future.

1. Introduction

Thermal power plants as well as energy-intensive industries like Poland's iron and steel sector have recently been facing a number of challenges such as rising fuel prices, potential geopolitical repercussions from the energy crisis, restrictions on the use of conventional fuels, increases in fuel prices as well as carbon taxes [1,2]. Current waste management systems, especially for waste not suitable for material recycling, are based on thermal treatment methods, particularly incineration or, as a last resort, landfilling [3]. To ensure continuous production at reasonable costs, the metallurgical industry must diversify gas fuel supplies by turning towards more future-oriented and environmentally friendly alternatives [4]. One of them is to utilize the potential of waste, which, when subjected to thermal processing [5], can provide valuable products, especially high-calorific gas, and in turn,

alleviate the ongoing energy crisis [6,7].

Waste, apart from incineration, may also be subjected to other methods classified as thermal conversion, such as pyrolysis [8] and gasification [9]. Therefore, thermal conversion methods have recently gained greater popularity [10,11]. Literature data indicate that among all the above-mentioned processes, pyrolysis is one of the most prospective, economic and effective methods of waste disposal [12,13]. Pyrolysis is considered as a chemical recycling process, and unlike incineration, it enables the recovery of both energy and hydrocarbon products in solid (carbon-rich), liquid and gaseous forms, such as pyrolysis oil and pyrolysis gas, as presented in Fig. 1 [14,15].

Pyrolysis gas, a gaseous product of thermal waste conversion, deserves special attention [16]. The energetic use of pyrolysis gas proposed in the article becomes important if this gas is obtained from non-biodegradable waste, such as plastics [17] and refuse-derived fuel

* Corresponding author.

E-mail address: monika.zajemska@pcz.pl (M. Zajemska).

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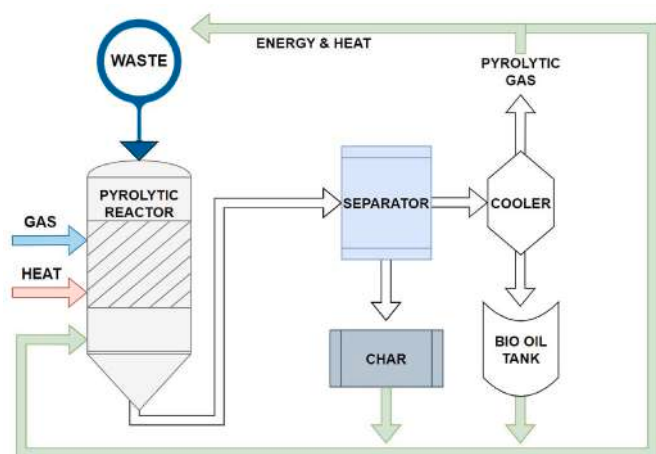


Fig. 1. Schematic diagram of waste pyrolysis process [15].

[8].

The pyrolysis process is carried out under inert conditions, typically in a nitrogen atmosphere in the absence of oxygen. Pyrolysis products, i. e. liquid and gas, can be utilized as alternative fuels in engines as well as combined heat and power plants [18]. Additionally, pyrolysis helps mitigate the issue of waste storage while reducing the emission of harmful substances and greenhouse gases that would be released uncontrollably during the landfilling of such waste or as a result of insufficient treatment of waste gases from its incineration [5,19].

A key advantage of the pyrolysis process is its flexibility in selecting operating parameters such as temperature, pressure and residence time [20,21] which ensures control of the share of the final products from this process [22]. In addition, pyrolysis is characterized by low emissions of carbon monoxide (CO) and carbon dioxide (CO₂), which make the process more ecological [8]. Moreover, as indicated in Ref. [23], the investment in a pyrolysis installation promises a quick return.

Pyrolysis has proven to be an environmentally friendly method for converting various solid waste, including biomass [24–26], plastics [27–29], mixtures of biomass and plastics [30,31], and refuse-derived fuel (RDF) [8,32,33], into valuable chemical products and fuels [34]. The presence of plastics in the waste stream during pyrolysis increases the calorific value of the resulting products, reduces the formation of oxygen and decreases the proportion of coke in the pyrolysis output [35,36].

Current pyrolysis gas management primarily involves using the gas produced during pyrolysis as a fuel to sustain the process's autothermal operation as detail in Ref. [37].

Another confirmed application of pyrolysis gas is its use as an alternative fuel in internal combustion engines [38].

The gas fraction produced at higher temperatures without a catalyst is characterized by a suitable calorific value (approximately 28 MJ/m³). In this way, pyrolysis gas could find a significant market, particularly in industrial and domestic boilers, where the demand for gaseous fuels is high. Additionally, it could be used in engines and gas turbines, enabling the production of both electrical and thermal energy [39,40].

A similar solution is the production of biogas (methane) through anaerobic fermentation in bioreactors. The gas produced is also intended for energy purposes, primarily for use in residential or agricultural buildings [41–43]. The main material processed in this type of solution is biomass waste. However, the advantage of the pyrolysis process over biofermentation lies in the broader range of waste materials that can be processed.

Hossain et al. [38] conducted a study where they successfully utilized pyrolysis gas as fuel in spark-ignition engines. The results showed that the same power output could be achieved as with natural gas, although engine operation was less stable. Liu et al. [44] pyrolyzed

sewage sludge, yielding approximately 52.36 % biochar and 46.40 % pyrolysis gas. The researchers proposed using the pyrolysis gas for direct combustion to generated heat which could support the pyrolysis process, with the exhaust gases for drying wet sewage sludge or generation steam. Pessoa Filho et al. [45] aimed to determine the optimal pyrolysis conditions for maximizing pyrolysis gas yield from solid plastic waste, and then to simulate the combustion of the gas. The results were highly promising, with the lower calorific values of the resulting gases being close to those of commercial combustible gases. Additionally, focusing pyrolysis on gas production and selecting appropriate parameters allowed for the generation of 98 % pyrolysis gas by volume from HDPE (High-Density Polyethylene) pyrolysis, which is a very promising outcome.

As the literature indicates, researchers are increasingly proposing and studying innovative ways for utilizing pyrolysis gas. However, no technology has yet been implemented on a large scale. The various methods for pyrolysis gas utilization are primarily applied at the pilot or laboratory scale. Identifying the most effective and economically viable solutions, along with promoting the technology on a broader scale would undoubtedly contribute to reducing fossil fuel extraction, lowering emissions, and managing previously unused waste.

The authors of this paper are the originators of a concept that involves integrating a pyrolysis reactor into the existing technological process of a metallurgical plant. Specifically, the reactor would be placed before the recuperator of the heating furnace used to preheat the feedstock before hot-working. This positioning of the reactor would allow the use of exhaust gas heat to raise the temperature of the pyrolysis reactor to as high as 900 °C. The originally proposed solution was developed for the gasification of torgas and published in the work by Szwaja et al. [5]. It is important to note that, according to Polish law, a system can only be classified as "pyrolysis" if it does not produce emissions higher than those from the combustion of natural gas, which limits the energetic potential of the pyrolytic gas. Therefore, a high degree of purification of the pyrolytic gas is essential in a pyrolysis installation to ensure that, when burned in an engine, it does not produce emissions higher than those of natural gas. Any exceedance of allowable emission levels results in the installation being classified as an "incinerator", and thereby making it subject to all applicable regulations. Thus, the method of purifying syngas, rather than the process occurring within the reactor itself, becomes critical in determining the classification of the installation. Consequently, for waste-to-energy plants employing pyrolysis, the proper purification of pyrolytic gas to eliminate harmful emissions is essential, which is associated with high costs. Therefore, alternatives are being sought to eliminate the need for costly gas purification without reducing the yield of gas from the pyrolysis reactor in favor of, for example, char. One such alternative is the use of hot pyrolytic gas to fuel a high-temperature heating furnace.

Continuous monitoring of the quality of produced steel is also a good practice, as it allows for temporarily halting production at the right time to quickly eliminate products that do not meet the required specifications. One of the most advanced methods for quality control of steel products is the acoustic emission method, as presented in studies [46–48]. Any action aimed at reducing the operational costs of the steel industry will impact both the environment and competitiveness in the marketplace.

Given the energy crisis, rising fuel and energy prices, and challenges related to managing problematic waste, the solution proposed in this paper presents an opportunity to mitigate these issues.

It should be emphasized that high-temperature pyrolysis (around 700–900 °C) is geared toward maximizing the yield of gaseous products, which can then be converted into electrical and thermal energy. It is also important to note that the most critical feature of a waste-to-energy conversion facility is its ability to achieve a POSITIVE ENERGY BALANCE, meaning that the energy output from the process is greater than the energy required to conduct the process itself.

Apart from the research presented in this article, the authors

conducted the literature analysis using the VOSviewer software that illustrates the network connections in bibliometric research related to the identified topics. The use of this tool complements traditional literature review methods. The software allowed to systematically analyse the vast body of literature, identify trends over time, and uncover subtle patterns that might otherwise be overlooked. This visual representation of bibliometric data, in addition to a comprehensive review of the literature, provided a more structured approach to confirming the relevance of the research gap. The authors utilized the program to query the Scopus database, searching for all scientific articles with titles containing the terms: *pyrolysis gas* or *pyrolytic gas*, and *energetic use* or *energy*. The program identified 458 articles that matched the selected phrases. The authors used the command:

"TITLE ("pyrolysis gas" OR "pyrolytic gas") ("energetic use" OR "energy") AND (LIMIT-TO (DOCTYPE , "ar") OR LIMIT-TO (DOCTYPE , "re"))"

The retrieved data were then exported to the appropriate file format and imported into VOSviewer. Based on the imported data, all co-occurrence connections of keywords in the selected articles were analyzed. The program found 4321 recurring keywords, with those appearing at least five times being present in 282 articles. As a result of this analysis, a keyword map for occurrences of at least 10 times, has been generated (Fig. 2).

As demonstrated by the above analysis, the topic of pyrolysis gas utilization has been widely researched. The authors further narrowed the scope of the keywords by adding the following terms: *pyrolysis gas* or *pyrolytic gas*, *energetic use* or *energy*, *iron and steel* or *steel and iron* or *metallurgy* or *steel industry*, to identify only those articles relevant to the topic under discussion. The Scopus database returned only four publications that met the specified criteria, and only two were related to the metallurgical industry. The authors used the command:

"TITLE ("pyrolysis gas" OR "pyrolytic gas") ("energetic use" OR "energy") ("iron and steel" OR "steel and iron" OR "metallurgy" OR "steel industry") AND (LIMIT-TO (DOCTYPE , "ar") OR LIMIT-TO (DOCTYPE , "re"))"

As this analysis shows, the topic of using pyrolysis products for energy purposes has been extensively studied. However, the innovative concept proposed by the authors of this paper remains largely

unexplored, making it a novel and pioneering area of research.

VOSviewer identified 458 publications addressing the issue of pyrolysis, but all these articles cover a wide range of pyrolysis applications across different fields. The application of pyrolysis in metallurgy to reduce furnace operating costs and manage waste is an extremely niche topic, which the authors of this publication aim to address and fill this research gap.

This paper presents a promising approach that relies on co-firing coprolysis gas (from biomass, plastic waste and RDF) with natural gas and coke oven gas in a pusher type metallurgical heating furnace in order to reduce the high cost of conventional fuels. In times of energy crises focused on conserving fossil fuels, the idea presented herein should be of considerable interest.

2. Methods

2.1. Materials

The materials used in production of the pyrolysis gas include lignocellulosic biomass in the form of alder wood (AW) and pine wood (PW) chips, along with polypropylene (PP) waste. Fig. 3 depicts the types and combinations of materials used in the present study. Two primary mixtures are highlighted: 58 % PP combined with 42 % PW and 58 % PP with 42 % AW. These mixtures were explored to investigate how different compositions contribute to the content of the pyrolysis gas.

The carbon, hydrogen, nitrogen and sulfur contents of these materials were determined using the Vario MACRO Cube CHNS analyzer (Table 1). The pyrolysis process of the considered materials was conducted in a reducing atmosphere (N_2/H_2 95 %/5 %) at the temperature of 1120 °C, with an automatic elemental analyzer from Elementar Analysensysteme GmbH. The calorific value of the analyzed biomass was determined by the calorimetric method in a constant volume calorimeter bomb. This value was calculated based on the temperature rise, calorimeter heat capacity and sample mass, and corrected by the value resulting from the combustion of auxiliary substances, i.e. the ignition wire.

2.2. Experimental stand for pyrolysis

The pyrolysis of a lignocellulosic biomass with PP waste mixture was

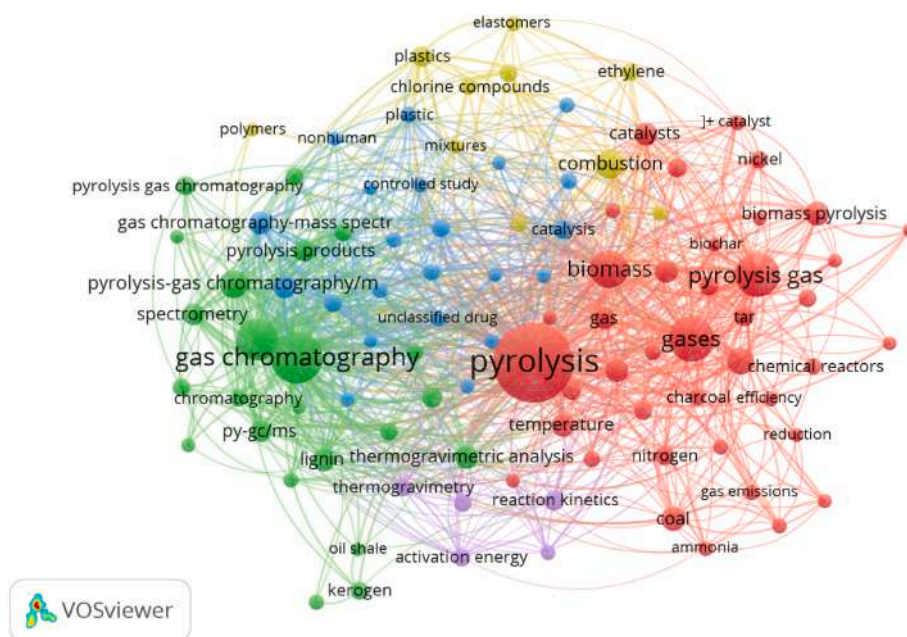


Fig. 2. Keyword map from the VOSviewer software.

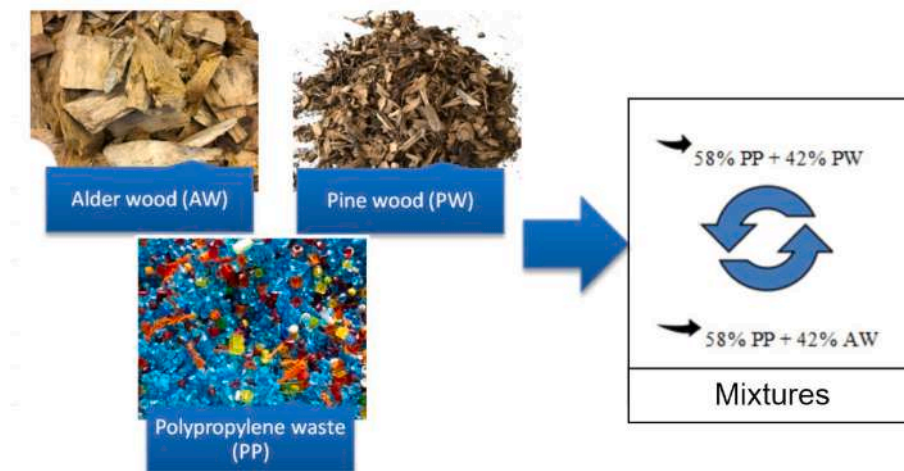


Fig. 3. Types of fuels used in the study.

Table 1

Proximate and ultimate analysis of pine and alder wood, PP.

Parameter	Unit	PP	Pine wood	Alder wood	Expanded uncertainty
Moisture content — W^a	wt%	0	3.13	4.5	0.1
Ash content — A^a		0	1.58	1.3	0.2
Volatile matter content — V^a		100	81.5	87.55	0.45
Carbon content — C^a		84.8	49.5	47.5	0.6
Hydrogen content — H^a		14.55	6.43	6.37	0.32
Nitrogen content — N^a		0.14	0.07	0.29	0.01
Sulfur content — S^a		0.23	0.06	0.15	0.01
Oxygen content — O^a		0.28	42.99	40.85	0.82
Heat of combustion — HHV	MJ/kg	45.80	20.22	19.62	0.20
Cellulose	wt%	—	41.75	35.45	1.5
Hemicellulose		—	25.29	28.30	0.6
Lignin		—	22.79	26.45	0.4

carried out on an experimental stand designed for the conversion of solid fuels in a stationary bed, described in detail in Ref. [8]. The core component of the setup was an electric furnace equipped with a steel retort, where the process of converting the mixture of biomass and polypropylene waste with a liquid and gas phase collection system took place. A schematic of the setup is shown in Fig. 4.

The studied waste, weighing 100 g, was placed in the steel retort and tightly closed. Nitrogen was fed from the bottom of the retort for about 15 min at a constant flow of 500 cm³/h in order to obtain inert conditions. After 15 min, the nitrogen flow was reduced to 100 cm³/h, then pyrolysis was initiated. The pyrolysis process was conducted at the temperature of 600 °C. The heating rate was kept constant at 10 °C/min in all the experiments. After the desired temperature was reached, the retort with the sample was held at the final temperature for 5 min (for temperature normalization inside the retort), then immediately removed from the furnace and finally cooled to ambient temperature. The analysis of gases such as CO, CO₂, H₂ and CH₄ was performed continuously, with the results reported as the average content of each gas over the duration of each pyrolysis test. In addition to automatic analysis, samples of the process gases were collected in sampling bags (Tedlar type) with a capacity of 25 L for subsequent chromatographic analysis. In this case, the results also constituted the sum of the components obtained during the process (Table 2).

2.3. Experimental stand of three-zone pusher furnace

The analysis of the benefits resulting from the energy use of pyrolysis gas was carried out for the metallurgical pusher type heating furnace adapted for the combustion of coke oven gas operating in the sheet rolling department of a steel mill. The design capacity of the furnace was 90 t/h and the installed capacity of the furnace was 72.3 MW. Fig. 5 presents the simplified scheme of the pusher furnace, while a detailed diagram is presented in the work of Szwaja et al. [5].

Such a type of furnace includes three heating zones, namely.

- pre-heating (900 °C),
- heating (1150 ÷ 1300 °C),
- compensation (1250 °C)

and is fired with natural gas or a mixture of natural gas and coke oven gas (Table 3). With regard to automation, the furnace has 105 burners mounted on the side walls and ceiling, and is separated into six control zones (Fig. 5).

3. Results and discussion

3.1. Proximate and ultimate analysis of fuel samples

The results of the proximate and ultimate analysis are summarized in Table 1. The tests were performed for individual fuel types.

As can be seen the maximum carbon content is observed in PP at 84.8 wt% while the minimum is found in alder wood at 47.5 wt%. Similarly, polypropylene (PP) waste exhibits the highest hydrogen content at 14.55 wt%, with alder wood containing the lowest hydrogen content at 6.37 wt%. Pine wood falls between these values, with a carbon content of 49.5 wt% and hydrogen content of 6.43 wt%. Additionally, the lower heating value (LHV) was estimated for all analyzed fuels and their mixtures (Fig. 6).

The (PP) waste was characterized by the highest LHV, that was over 45 MJ/m³. The lowest LHV, being over three times lower than LHV of PP, was observed in case of alder wood.

3.2. Analysis of pyrolysis gas

Table 2 presents the compositions of the obtained pyrolysis gases for the individual fuels and their blends.

As presented in Table 2, the pyrolysis gas generated from polypropylene (PP) waste is characterized by the highest content of C₂H₄, C₂H₆, C₃H₆, C₃H₈ and C₄H₁₀. The highest content of H₂ was observed in

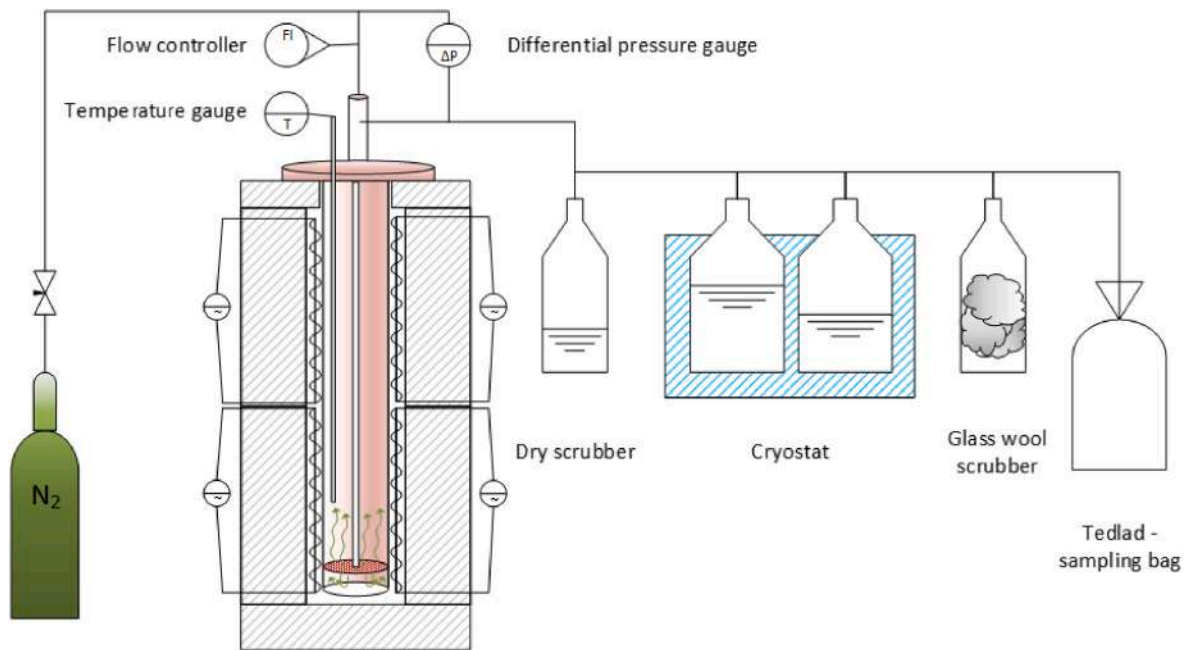


Fig. 4. Test stand for pyrolysis of mixture of lignocellulosic material and PP waste.

Table 2
Composition of pyrolysis gas for investigated waste mixtures.

Units	H ₂	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂
	Mol %									
PP	1.99	0.571	0.76	10.31	5.14	9.24	62.28	6.92	2.76	0.01
AW	7.27	31.20	38.98	14.37	0.59	1.08	0.33	0.26	0.04	0.03
PW	10.28	29.44	30.07	24.09	0.48	1.11	0.33	0.22	0.04	0.02
PW + PP	6.49	20.82	22.80	14.88	1.97	3.81	11.32	1.60	1.07	0.11
AW + PP	8.19	22.99	27.16	17.45	2.64	4.73	11.14	1.95	0.84	0.03

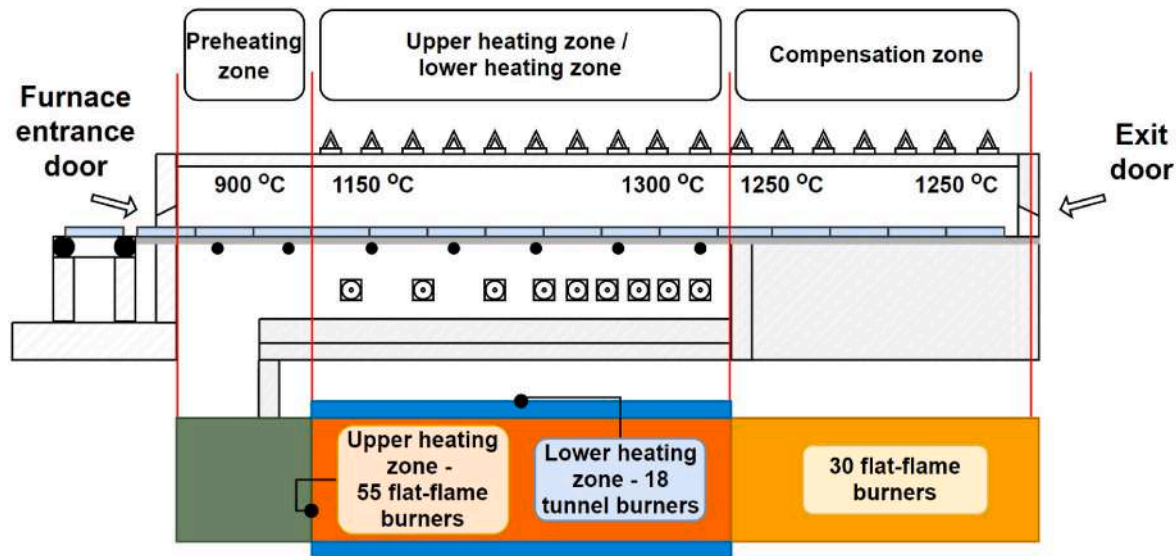


Fig. 5. Simplified diagram of three-zone pusher furnace [5].

case of pine wood, as well as the blends of alder and pine wood. In turn the greatest share of carbon monoxide was indicated in pyrolysis gas from alder and pine wood used individual.

3.3. Analysis of gases feeding heating furnace

As mentioned in previous section, the pusher type furnace was generally fired with natural gas or a mixture of natural gas and coke oven gas, which composition is presented in Table 3.

Table 3
Chemical composition of gases feeding heating furnace.

Unit	CH ₄	H ₂	C _m H _n	N ₂	CO ₂	CO	O ₂	LHV
	%							MJ/m ³
Natural gas ^a	97.1	–	1.7	1.1	0.1	–	–	36.25
Coke oven gas ^b	25	58	3	4	2.5	7	0.5	17.5

^a Composition of gas supplied to the steelworks by PKN Orlen

^b Composition of gas supplied to the steelworks by the local coking plant.

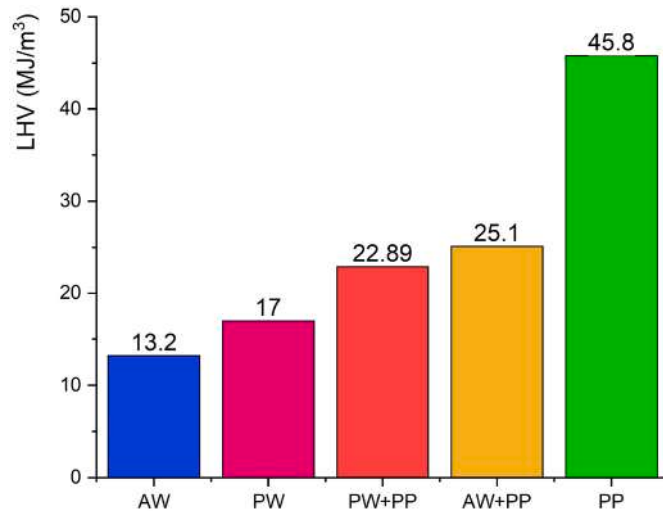


Fig. 6. LHV of studied fuels and their mixtures.

The fuel prices listed in Table 4 were used to calculate the costs of operating the metallurgical furnace, while Table 5 presents the gas consumption depending on the furnace capacity.

The following assumptions were used for these calculations.

- share of coke oven gas at the level of 1726 m³/h (maximum gas yield from coking plants),
- share of natural gas depending on demand (Table 6),
- share of pyrolysis gas for three variants (Table 6),
- continuous operation of the furnace 24 h a day for 30 days,
- natural gas and coke oven gas prices used for the calculations,
- cost of pyrolysis gas was assumed as zero.

The savings were calculated from Relationship 1.

Table 4
Prices of individual fuels.

Particular months of 2022	Natural gas		Coke oven gas	
	LHV	Price	LHV	Price
	MJ/m ³	Euro/m ³	MJ/m ³	Euro/m ³
January	36.2	0.94	17.3	0.29
February	36.1	0.90	17.4	0.28
March	36.3	1.53	17.5	0.48
April	36.3	1.18	17.6	0.37
May	36.0	1.01	17.5	0.32
June	36.0	1.15	17.6	0.36
July	36.4	1.98	17.7	0.62
August	36.2	2.63	17.6	0.82
September	35.9	2.18	17.7	0.69
October	36.1	0.96	17.5	0.30
November	36.6	1.07	17.3	0.33
December	36.5	1.37	17.3	0.43
Average price for the year	36.3	1.41	17.5	0.44

*Euro exchange rate: 1 EUR = 4.68 PLN, average value from 2022, price source <https://tge.pl/gaz-rdn>.

Table 5
Consumption of selected gaseous fuels depending on capacity of pusher furnace.

Capacity [t/h]	Natural gas consumption [m ³ /h]	Coke oven gas consumption [m ³ /h]
50	2291	–
	1458	1726
70	2708	–
	1875	1726
90	3125	–
	2291	1726
Furnace operation time [h]	6564	

The gas mass fluxes of natural gas (NG), coke oven gas (COG), as well as pyrolysis gas (PG) for the capacity of a pusher furnace ranging from 50 to 90 t/h, presented in Table 6, were assumed for the calculations.

Table 6
Gas loads taken for calculations.

Gases	Type of fuel			Gas stream		
	NG	COG	PG	NG	COG	PG
	Share %			m ³ /h		
Capacity 50 t/h						
NG	100	–	–	2291	–	–
NG/COG	46	54	–	1458	1725	–
NG/COG/PG	37	52	11	1240	1725	345
NG/PG	84	–	16	1850	–	345
Capacity 70 t/h						
NG	100	–	–	2708	–	–
NG/COG	52	48	–	1875	1725	–
NG/COG/PG	44	46	10	1650	1725	356
NG/PG	88	–	12	2300	–	323
Capacity 90 t/h						
NG	100	–	–	3125	–	–
NG/COG	57	43	–	2291	1725	–
NG/COG/PG	50	41	9	2070	1725	351
NG/PG	89	–	11	2900	–	356

$$\text{Savings} = \frac{\text{Monthly operating cost of natural gas furnace in Euro}}{\text{Monthly cost of furnace operation for NG + COV + PG mixture in Euro}} \quad (1)$$

The average price in 2022 of natural gas was 1.41 Euro/m³, while in case of coke oven gas it was over three times less, i.e. 0.44 Euro/m³.

In Table 5 the consumption of the aforementioned gas fuels was determined for the capacity of a pusher furnace ranging from 50 to 90 t/h and chemical power (heat from gas combustion and heat entering with hot air) ranging from 23.08 to 31.47 MW.

3.4. Wobbe index analysis

An important factor in the combustion of gas-fuel mixtures is the Wobbe index, which is an indicator of the interchangeability of fuel gases. Based on the following relations (2 and 3) the Wobbe number values were calculated for the investigated gas compositions and are displayed in Table 7.

$$\text{Wobbe index} = \frac{\text{Heating value}}{\sqrt{\text{Specific gravity}}} \quad (2)$$

where:

$$\text{Specific gravity} = \frac{\text{density of fuel gas}}{\text{density of air}} \quad (3)$$

Thanks to the Wobbe index, one can easily classify a given fuel mixture as a local fuel that can be distributed via a local network or as a commercial fuel that can be distributed for municipal, industrial and

Table 7

Wobbe Index for researched fuel mixtures.

Fuel & mixtures	Unit	Low Wobbe index	High Wobbe index
Fuel			
NG	MJ/m ³	47.6	52.8
COG		30.8	34.7
AW + PP		27.3	29.5
PW + PP		24.5	26.4
Mixtures (participation %)			
50 t/	MJ/m ³	39.2	43.7
h NG/COG (46/54)			
h NG/PG (84/16)		42.5	47.0
h NG/COG/PG (37/52/11)		35.8	39.8
70 t/	MJ/m ³	40.2	44.8
h NG/COG (52/48)			
h NG/PG (88/12)		43.7	48.3
h NG/COG/PG (44/46/10)		37.2	41.3
90 t/	MJ/m ³	41.0	45.7
h NG/COG (57/43)			
h NG/PG (89/11)		44.0	48.7
h NG/COG/PG (50/41/9)		38.3	42.5

engine fuel purposes (Table 7).

The obtained results clearly show that the proposed gas mixture streams can be classified as fuel intended for local distribution. All the proposed mixtures are in the highest group of local fuels (Lw – see Table 8), whose calorific value of the upper Wobbe index does not fall below 39 MJ/m³. All of the above-mentioned mixtures of natural gas and coke oven gas are successfully combusted in the described furnace, which confirms the possibility of co-firing all three gases. The lower Wobbe index is compensated by a correspondingly larger flow of a given fuel, without a loss of burner power.

3.5. Concept of using pyrolysis installation in the technological line of pusher type metallurgical furnace

In the proposed solution (Fig. 7), it was assumed that the steelworks is equipped with a pyrolysis reactor with a capacity of approximately 1000 kg/h for processing waste or materials of biomass origin with a maximum humidity of 10 % by mass. The process temperature should fluctuate between 800°C–900°C to obtain the expected amount of pyrolysis gas. The process is aimed at producing biochar, while the resulting pyrolysis gas is treated as waste gas, partially used to heat the reactor.

A reactor with a 1000 kg/h capacity and a processing capacity of 6564 h annually is expected to cost roughly 5,300,000 EUR (CAPEX). Depending on the type of waste and the calorific content of the products derived from the input material, the pyrolysis gas can account for more than 50 % of the input mass.

The concept involves positioning the pyrolysis reactor before the recuperator, allowing the exhaust gases exiting the heating furnace to reach a sufficiently high temperature (approximately 900 °C) to heat the reactor to the required level. Additionally, the heat from the exhaust gases is utilized for the preliminary drying and preheating of the material intended for the pyrolysis process. The gas fraction produced

Table 8

Classification of gases according to Wobbe index value.

Group	Symbol	Symbol subgroup	High Wobbe index, [MJ/m ³]	Main compound	Basic use
Nitrided	L	Lm	23 ÷ 27	CH ₄ , N ₂	Local fuel
		Ln	27 ÷ 32.5	CH ₄ , N ₂	
		Ls	32.5 ÷ 37.5	CH ₄ , N ₂	
		Lw	37.5 ÷ 45	CH ₄ , N ₂	
High-calorie	E		45 ÷ 54	CH ₄	Network fuel

during the process (without cooling or condensation) is then directed straight to the main pipeline and subsequently to the burners. The combustion system is equipped with regulators that control the flows of primary and secondary gas in real time, based on the measured calorific value.

In order to estimate the consumption of coke oven gas and/or pyrolysis gas instead of natural gas, the so-called conversion factor for changing from natural gas to coke oven gas or pyrolysis gas was used, i.e.

$$n = \frac{LHV_{NG}}{LHV_{COG/PG}} \quad (4)$$

where:

LHV_{NG} - calorific value of natural gas MJ/m³,

$LHV_{COG/PG}$ - calorific value of substitute gas, i.e. coke oven gas and pyrolysis gas MJ/m³.

The determined values of the above-mentioned coefficient $LHV_{COG/PG}$ are 2.07 for coke oven gas and 1.58 for pyrolysis gas (PW + PP). By analyzing the consumption of the above-mentioned gases and their prices, the costs of one month's operation of a pusher type furnace were compared.

On-site inspections and consultations with experts from the metallurgical plant analyzed in the article confirmed the feasibility of integrating the pyrolysis reactor into the existing installation without incurring additional modernization costs. Besides the primary product of high-temperature pyrolysis, pyrolytic gas, a solid fraction known as char is also produced, which will be utilized within the plant as a substitute for coke. Sankey diagrams illustrating the mass and energy flow for the tested materials are presented in Figs. 8 and 9.

For the above-mentioned fuel variants, the monthly savings resulting from replacing natural gas with pyrolysis gas were calculated. Table 9 displays the monthly operating costs of the furnace for the analyzed variants for different furnace capacities. For the calculations, the average prices of natural gas and coke oven gas in 2022 were used (see Table 4).

Fig. 10 illustrates the potential savings that can be achieved by partially replacing natural gas with coke oven gas and pyrolysis gas in co-combustion scenario. The data indicates that the savings can range from 16.4 % to 22.2 % when utilizing a blend of natural gas, coke oven gas and pyrolysis gas, highlighting the economic benefits of this approach.

3.6. Economic analysis

The calculation results demonstrate that the selected gases can be successfully co-combusted in a pusher type reheating furnace if they are supplied in the appropriate quantity. To enable the direct supply of pyrolysis gas to the furnace burners, a pyrolysis installation must be included into the process line. For this modernization to take place, its purchase must be economically feasible. The local production of energy, heat or biofuels plays an important role in conserving energy, the production of which does not have to use fossil fuels. The economic efficiency of the proposed installation depends on the type of co-combusted fuels and the capacity at which the furnace operates.

The economic evaluation of the selected pyrolysis installation depends on the total investment costs, operating costs and revenues. To assess economic efficiency, the method of analyzing the net present value (NPV) was chosen, which has been successfully employed to assess profitability in similar investments [49–51]. NPV presents the value of an investment based on the required rate of return, the operational lifetime of the device, investment risk and time to achieve revenue.

The value of the discount rate was set at 5,85 % (in accordance with the National Bank of Poland recommendations). The operational lifetime of the installation is 20 years, and the economic assessment was calculated for a period of 6 years. Cash flows were calculated on the basis of savings obtained from the co-combustion of coke oven gas and

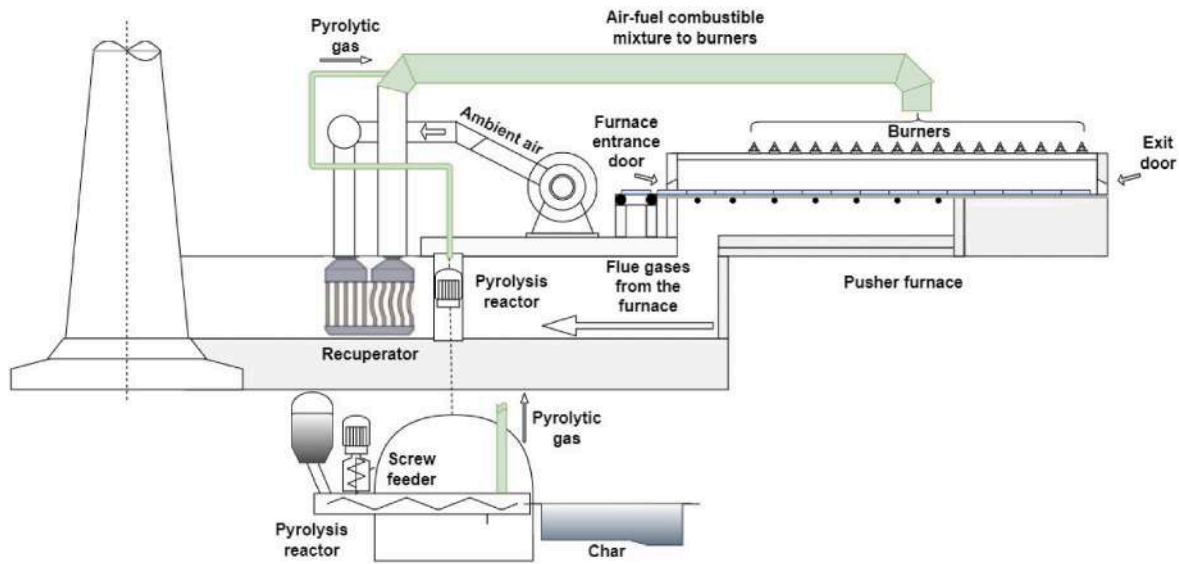


Fig. 7. Concept of proposed solution (Szwaja et al. 2021; Zajemska et al., 2023).

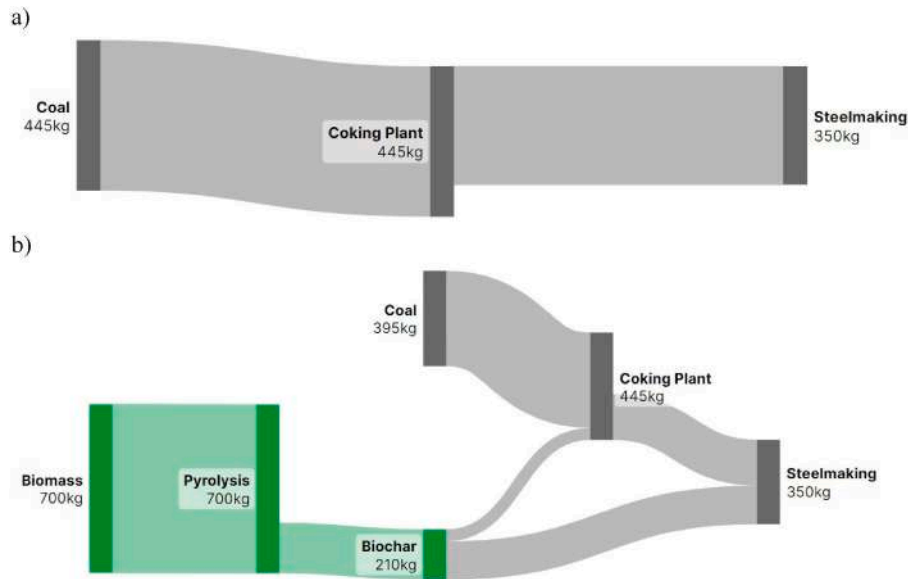


Fig. 8. Sankey diagram for carbon in metallurgy: a) conventional pathway utilizing fossil coal, b) alternative pathway utilizing biochar.

pyrolysis gas, calculated for subsequent periods (years). All the assumptions for calculating NPV are summarized in Table 10.

The NPV coefficient was calculated using the formula:

$$NPV = \sum_{i=1}^n \frac{CF_i}{(1+r)^i} - I_0$$

where.

- CF_i – cash flows
- r – required rate of return
- n – number of periods
- I_0 – value of initial expenditure

The assumed operational lifetime of the installation coincides with the operational lifetime of the pusher type reheating furnace. The operational lifetime of the installation was set at 20 years. Investment costs were estimated based on the authors' own calculations, data

provided by the local steelworks and the company operating the selected pyrolysis installation. The total investment cost was EUR 5,300,000 and the operating costs were EUR 700,000,

It was also assumed that the investment would be financed from the funds of the company managing the local steelworks, which eliminates the need to take out a loan and additional costs. The investment return rate was assumed to be 10 %.

The main assumption of the NPV indicator is the profitability of the investment, thus it should be $NPV \geq 0$. The investment payback period was calculated for all the assumed fuel mixtures and three furnace capacities. The obtained results are presented in Figs. 11–13.

According to the economic analysis, pyrolysis gas can be a competitive substitute for natural gas and coke oven gas. For all the analyzed variants, i.e. different furnace capacities and different fuel mixture compositions, the monthly operating costs of the furnace were significantly lower than for the combustion of natural gas only (Table 9). The monthly operating cost of the furnace for all the variants was lower in relation to natural gas by 12.7 %–22.2 % for the furnace capacity of 50 t/

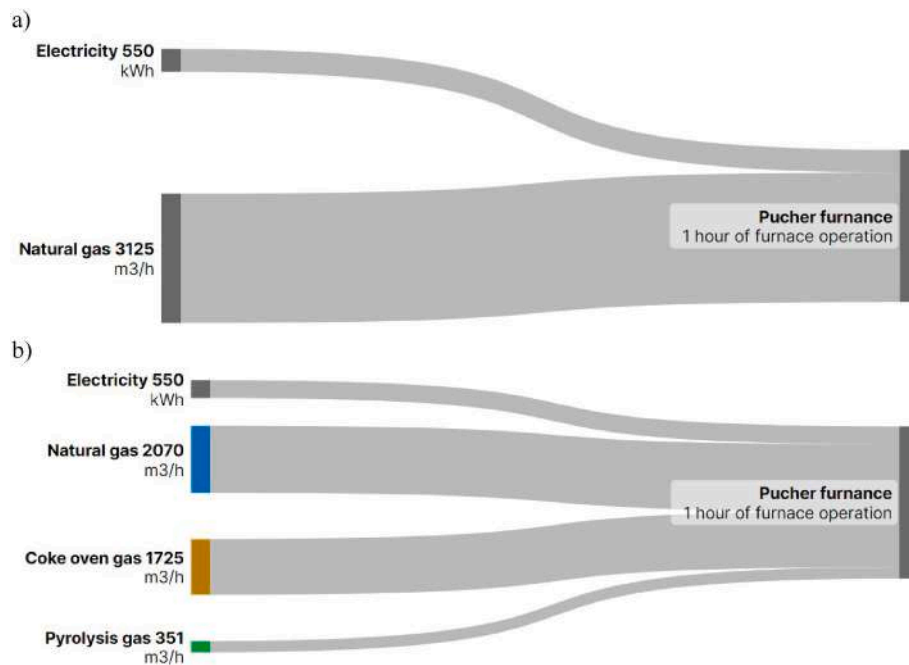


Fig. 9. Sankey diagram for the use of electricity and gases: a) conventional pathway utilizing electricity, b) alternative pathway utilizing electricity, natural gas, and supplementary gases.

Table 9

Consumption and costs of natural gas for various fuel variants (furnace capacity 50/70/90 t/h).

Gases	Cost	
	Consumption m ³ /month	EURO/monthly Average price ^a
Capacity	50 t/h	
NG	1,650,002	2,323,400
NG/COG	2,292,689	2,028,176
NG/COG/PG	2,384,565	1,806,820
NG/PG	1,580,868	1,875,615
Capacity	70 t/h	
NG	1,949,997	2,745,829
NG/COG	2,592,689	2,450,612
NG/COG/PG	2,687,369	2,222,497
NG/PG	1,888,747	2,331,846
Capacity	90 t/h	
NG	2,250,000	3,168,269
NG/COG	2,892,689	2,873,048
NG/COG/PG	2,985,967	2,648,312
NG/PG	2,344,550	2,940,153

^a Average price of natural and coke oven gas for 2022.

h and decreased with growing capacity: for 70 t/h it was 10.78 %–19.1 % and for 90 t/h it was 9.3 %–16.4 %. Comparing the operating cost of a furnace fired with the NG/COG mixture with the NG/COG/PG mixture and with the NG/PG mixture, it can be seen that for all the variants, the highest return on investment can be expected from a furnace with the capacity of 50 t/h. Comparing the savings resulting from the use of the mixtures for different furnace capacities (Fig. 10) calculated based on Relationship 1, it can be seen that each of the analyzed variants is beneficial.

4. Summary

The steel sector is one of the most energy-intensive industries, therefore considerable efforts are being made around the world to improve its energy efficiency and reduce greenhouse gas emissions [1,

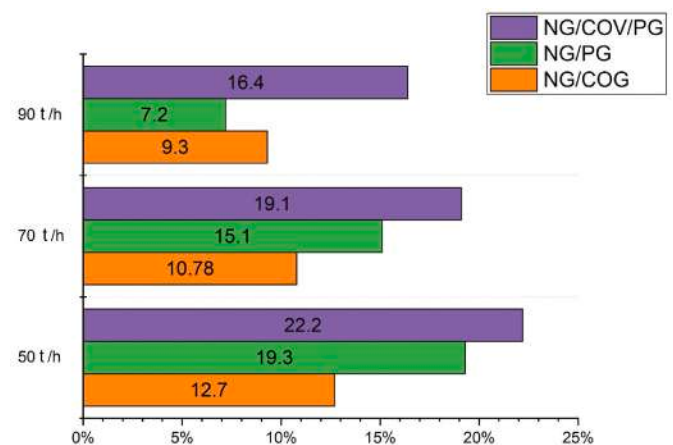


Fig. 10. Comparison of savings for analyzed variants with co-combustion, %.

Table 10

Selected assumptions used to calculate NPV.

Parameters	Unit	Value
CAPEX	Euro	5,300,000
OPEX	Euro	700,000
Annual working time	hours	6564
Operational lifetime	years	20
Payback time	years	6
Discount rate, r	%	5.85
Unit price for management of 1 t of RDF	Euro	32.05
Unit of environmental cost	Euro/year	642
Monthly operating expenses	Euro/month	6439

52]. This article presents an innovative approach to utilize in the iron and steel industry the potential of calorific waste as a promising path not only towards sustainable production and waste management, but above all towards decarbonization. The research conducted by the authors shows that.

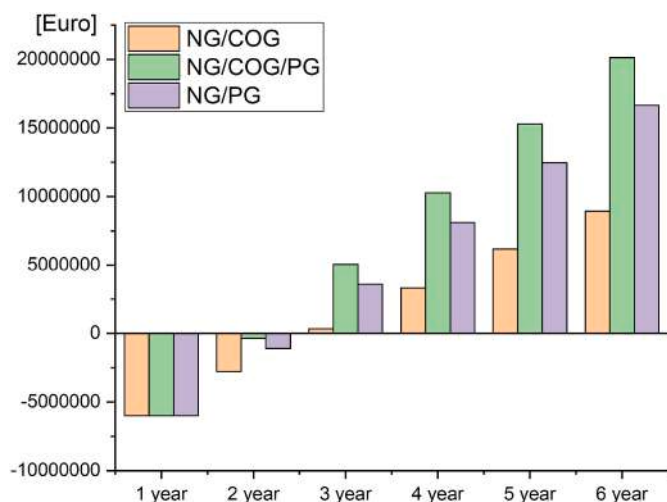


Fig. 11. NPV from co-combustion of various gas mixtures for furnace capacity of 50 t/h.

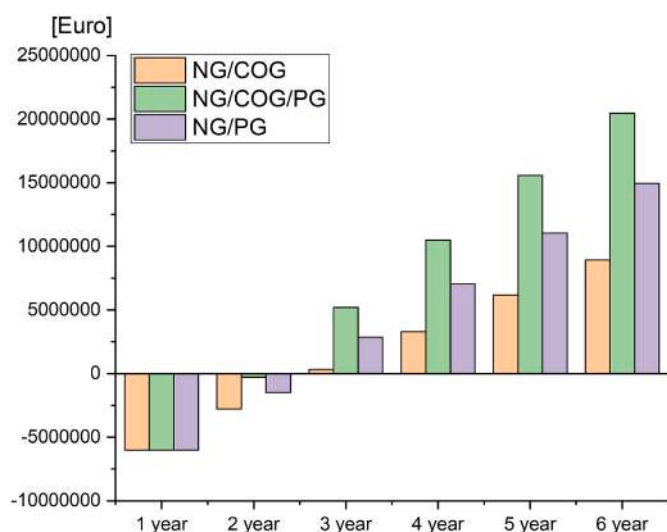


Fig. 12. NPV value from co-combustion of various gas mixtures for furnace capacity of 70 t/h.

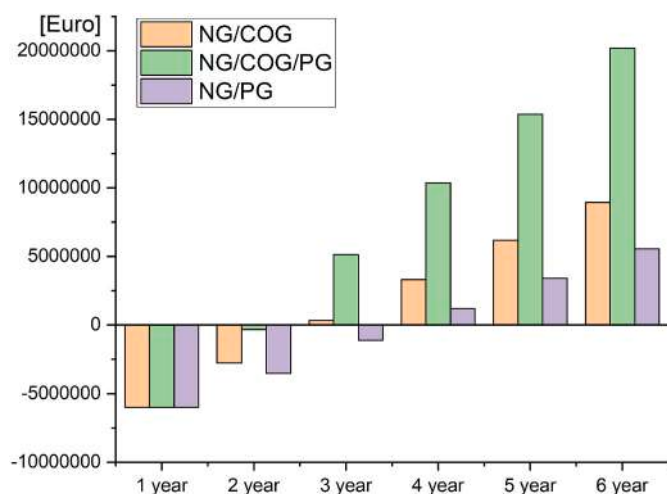


Fig. 13. NPV value from co-combustion of various gas mixtures for furnace capacity of 90 t/h.

- the addition of at least 9 % pyrolysis gas to the fuel mixture can reduce the operating costs of a pusher type reheating furnace by over 16 % per month compared to the operating costs of a furnace burning only natural gas,
- the addition of 16 % pyrolysis gas to the fuel mixture is able to reduce the operating costs of the pusher type reheating furnace by over 19 % per month compared to the operating costs of a furnace burning only natural gas,
- the greatest savings can be achieved with a furnace capacity of 50 t/h due to the fact that the share of pyrolysis gas in this case is the highest,
- the most financially advantageous scenario is the co-combustion of natural gas, coke oven gas and pyrolysis gas. According to the authors' calculations, at each of the three furnace capacities, the financial benefits are the greatest.

Waste is an important energy resource, especially in the most energy-intensive industries such as the iron and steel industry. The authors of the article, based on the results of their own research and the latest literature reports, emphasize the role of thermal waste conversion products, in particular pyrolysis gas, in the energy transformation of the global steel industry. The interest of steel industry enterprises in the energy use of waste prompts intensified research in this area.

The authors, as well as their co-operators from LIBERTY Steel Poland, see an application potential of the solutions proposed in the article, which will result in.

- a reduction in the consumption of conventional fuels, in particular natural gas, while providing measurable economic benefits,
- the possibility of using pyrolysis gas in practice by means of a direct gas supply to the chamber or with heated air after modernizing the furnace automatics,
- the ability of all the gas produced during the pyrolysis process, together with the non-condensed oil fraction, to be utilized for energy purposes; it will be supplied continuously during the pyrolysis process,
- the possibility of supplying gases with different calorific values to the furnace owing to the presence of a regulating calorimeter that continuously regulates the streams of the supplied gases,
- the ability to use the heat from the exhaust gas to heat the waste in the pyrolysis reactor, increasing the efficiency of the charge heating process at the same time.

The proposed solution is economically viable not only due to the savings that can be obtained in connection with the combustion of pyrolysis gas, but also owing to the amount of waste that can be processed, which provide other alternative fuels.

5. Conclusion

The authors have thoroughly analyzed the challenges and issues faced by waste-to-energy plants in Poland that utilize the pyrolysis process. One such challenge is the proper selection of the reactor. One plant in Poland tested several different solutions (e.g. Biogreen reactors by ETIA company with Spirajoule technology), where the energy balance was negative. The Biogreen reactors, powered by electricity, consumed significant amounts of energy for heating, maintaining, and running the process. Furthermore, the design of the reactor and the technology employed did not offer a means to improve this balance.

Data obtained for the purposes of this article, provided by a Waste-to-Energy Facility in Poland, indicate that depending on the type of feedstock, the demand for electrical energy is approximately 0.5–1.1 kWh/kg of processed feedstock. The more complex the waste and the more complicated its chemical structure, the more energy is required to break the bonds. For instance, the energy demand for RDF is approximately 1.0–1.1 kWh/kg, whereas for biomass, it is about 0.5–0.7 kWh/kg.

Below is an example of the balance for RDF waste:

From 1 ton of RDF waste with a calorific value of approximately 23 MJ/kg dry matter (dry waste, maximum 10 % moisture content), about 2 MWh of electrical energy and 4 MWh of thermal energy are obtained. Part of the electrical energy is cycled back into the process, so 1.1 MWh of electrical energy is returned to power the process, while the remaining surplus of approximately 0.9 MWh of electrical energy can be sold to the grid or used on-site to power other machinery. The thermal energy, depending on the efficiency of utilization, can be used for waste drying, heating facilities, heating water, or can also be sold to the district heating network, stabilizing the grid (industrial plants are often located far from main heating plants, typically at the peripheries of district heating networks, so the installation of distributed cogeneration positively impacts grid parameters).

On the revenue and avoided cost side, the following can be assumed.

- No need to purchase electrical energy from the grid in the amount of the surplus produced (i.e. approximately 0.9 MWh per 1 ton of processed RDF), or, if there is no need to utilize it on-site, the sale of this energy to the grid.
- No need to purchase thermal energy in the amount of approximately 4 MWh per 1 ton of processed RDF, or, if there is no need to utilize it on-site, its sale to the grid.
- No gate fees or transport costs for RDF to cement plants/incinerators, as the RDF fuel can be utilized on-site within the Regional Municipal Waste Processing Plant.

Operating costs include the purchase of consumables, internal transportation, operator personnel, char disposal, depreciation, and others,

The market price of such installations for a processing capacity of 1 t/h is approximately 4.3–5.3 million EUR net. It is assumed that the payback period for such an installation is around 4–6 years. An installation with a negative energy balance (like Biogreen) would never pay off.

Given the above, it should be emphasized that the advantage of the proposed solution is the utilization of all the products of the pyrolysis process within a single facility, with the innovative aspect being the energetic utilization of pyrolytic gas along with the condensable fraction, without prior purification. The solid product of pyrolysis in the form of char can serve as a substitute for coke, which is the subject of numerous publications, including those by the authors of this article [34].

The implementation of the concept proposed by the authors will result in reduced operating costs for the metallurgical furnace, which will translate into competitive pricing for steel products (compared to countries like Belarus or China, which do not bear the costs of CO₂ emissions trading) and environmental benefits through waste management, including the problematic RDF fraction in Polish conditions. Market analysis indicates that for most Regional Municipal Waste Processing Plant, RDF "disposal" is more of a cost than a revenue stream. Even if today the sale of RDF generates some profit, in the next 2–3 years, thermal conversion facilities expect an increase in the cost of disposing of 1 ton of this waste. In this regard, the steel industry can be a good place to utilize RDF waste, with its complete processing and management. Summarizing, the use of RDF waste in the pyrolysis process, for the production of pyrolysis gas and biochar, which will be completely used at the place of production (steelworks), will contribute to reducing the operating costs of the steel industry and to the waste management, which has not yet found a permanent recipient.

CRedit authorship contribution statement

Magdalena Skrzyniarz: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marcin Sajdak:** Writing – review & editing,

Formal analysis. **Anna Biniak-Poskart:** Writing – review & editing, Formal analysis. **Andrzej Skibiński:** Writing – review & editing. **Artur Maroszek:** Formal analysis, Data curation, Conceptualization. **Paweł Niegodajew:** Writing – review & editing, Formal analysis. **Monika Zajemska:** Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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