TWO-STAGE GASIFICATION PROCESS OF SOLID ORGANIC COMPOUNDS

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Cercetarea ale carei rezultate sunt prezentate în acest articol a fost axată pe gazeificarea în două trepte, la temperatura înaltă sub atmosfera de vapori, la presiune atmosferică, pentru transformarea compuşilor organici solizi cu recuperarea potenţialului energetic maxim urmărindu-se transformările produselor în timpul procesului şi influenţa lor asupra rezultatelor finale. Lucrarea a avut ca scop corelarea celor două stadii ale procesului de gazeificare secvenţială, evidenţiindu-se dependenţa dintre parametrii de proces şi cineticile de reacţie. Această abordare are la baza influenţa diferitelor structuri fizico-chimice ale produselor şi parametrii de devolatilizare-carbonizare: presiune, temperatură, perioadă de tratare, asupra procesului de formare a cocsului şi caracteristicilor sale fizice. În plus, au fost investigate avantajele procesului de piro-gazeificare în două trepte, comparativ cu gazeificarea directă.

The research focused on two-stage high temperature gasification under steam atmosphere, at atmospheric pressure conducted organic solid compounds for maximum energy potential recovery with respect to product transformation during the process and its influence on final results. The work aimed to establish the dependence of second gasification stage on the first devolatilization one together with the connection: process parameters – reactions kinetics. The approach was justified by the products different physical-chemical structures and carbonization parameters: pressure, temperature and residence time influence on the char formation and its physical characteristics. Furthermore the second reason for this approach was the advantages of two-stage pyro-gasification process, compared to direct gasification one.

Keywords: pyrolysis, gasification, kinetics, solid fuel

1. Introduction

The two-stage pyro-gasification process could offer solutions to technological problems for heterogeneous organic mixtures thermal processing with alternative fuel generation together with other technological benefits. The pyro-gasification is a stable process using a homogenous product in the second stage of the reaction - the pyrolysis char - a carbon and inert base product. In addition to that, the continuous mechanical stirring of the char advancing in the

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installation (based on different types of products: paper, cardboard, vegetal, plastic, with different porosities, specific surface) makes it more homogeneous and it can be assimilated to coal with a sensible low volatile content. The high friability of this product combined with the movement throughout the installation, involves the grinding of the char and the particles size reduction, increasing the specific surface and the gasification reaction rate leading to syngas conversion efficiency increase. To establish the first stage - pyrolysis process parameters influence on the char characteristics with respect to gasification stage we used wood and PET. The results can be used in different solid waste treatment using thermal-chemical processes such as pyrolysis and gasification conducted at atmospheric pressure. Both pyrolysis and gasification present undeniable advantages concerning the CO_2 / treated waste rate and dioxins formation and are the alternative for a safer waste thermal treatment. The high treatment temperatures and the massive presence of the oxygen facilitate the nitrogen toxic components and the flying ash transport (heavy metals), forcing the industrials to high efficiency and costly flue gas treatment utilities. Nevertheless the direct gasification of a heterogeneous solid waste or mixture involves process-operating difficulties due both to product heterogeneity and process instability. Therefore the two-stage gasification process results presented in this study may offer answers for the solid waste based on two main compounds: cellulose and polyethylene.

2. Experimental setup

The installation is a cylinder fixed bed reactor. An electric resistance externally heats the tube reactor made of refractory steel. The electric heating system offers the advantage of precise heating rate and constant temperature period control. The treated sample is introduced within a refractory longitudinal steel crucible in the active zone.

The reactor tube has two gas inlets for different experimental conditions: air, inert gas (nitrogen) or steam. These two inlets have flow regulators that give the possibility to modify the treatment process configuration.

At the opposite extremity of the treatment gas inlets there is the exhaust to the analyser for the gas generated during the treatment process. A regulator controls the pressure inside the tube.

The treatment atmosphere can be oxidant or reductive on choice, introducing air or nitrogen. For gasification experiments we used a constant flow of steam in combination with nitrogen as vector gas and for the flow control.

The treatment temperature can take any value between 100°C and 1200°C.
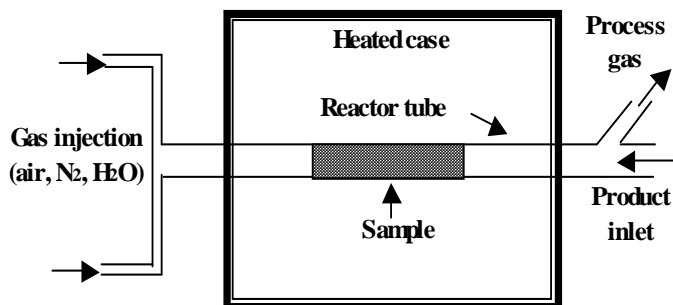
Fig. 1. Functional schema of tubular reactor.

The products used in our experiments were dried pinewood and PET. Compared to pyrolysis and gasification of lignocelluloses, the presence of high volatile components as plastics and rubber modifies the reaction kinetics, therefore we also used mixtures of these products.

3. Results and discussions

Influence of char heterogeneity and carbon content
Figure 2 presents the variation of CO_2 and CO during the pendant vapour-gasification for 2 constituents: wood (pine) and PET (grinded plastic bottle) at 1000°C and 1 g/min steam mass rate flow. This variation corresponds to char fixed carbon consumption and consequently to masse reduction rate, because CO and CO_2 are the main constituents that contain C in syngas.

For the mixed sample we used 1 gram of wood char + 1 gram of PET char. The char was produced by atmospheric pyrolysis treatment at 450°C. The residence time of pyrolysis was 15 minutes. We notice the different kinetics for each product. For the mixture the global kinetic is obtained by superposition of the components variation curves.

The required period for the complete gasification of the wood char is about 9 min, compared to plastic 15 min. The char structure strongly influences the process kinetics. The products based on plastic require a residence time with about 66% longer than the cellulose based products. For mixtures, the residence time is imposed by the product with the slowest kinetic. The factors that mainly influence the reactions speed are multiples and rather difficult to quantify. Among them we mention the porosity and specific surface. To clearly indicate the influence of these characteristics a detailed study is necessary that does not make the object of the present work.
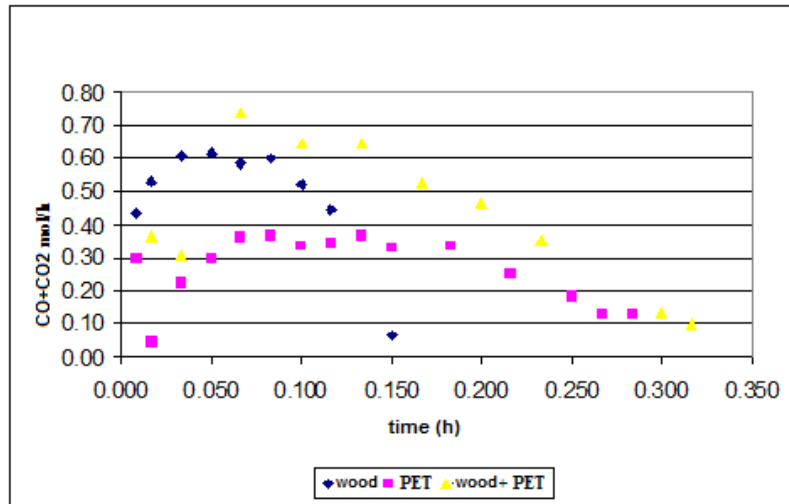
Fig. 2. The variation of CO2 and CO during the gasification applied to wood and PET char:
pyrolysis at 450°C for 15 min, gasification at 1000°C, 1gH2O/min.

With respect to carbon content influence, as we notice in the figure 3, the kinetics of the fixed carbon consumption for both products are similar. The two variation curves are quasi-parallels.
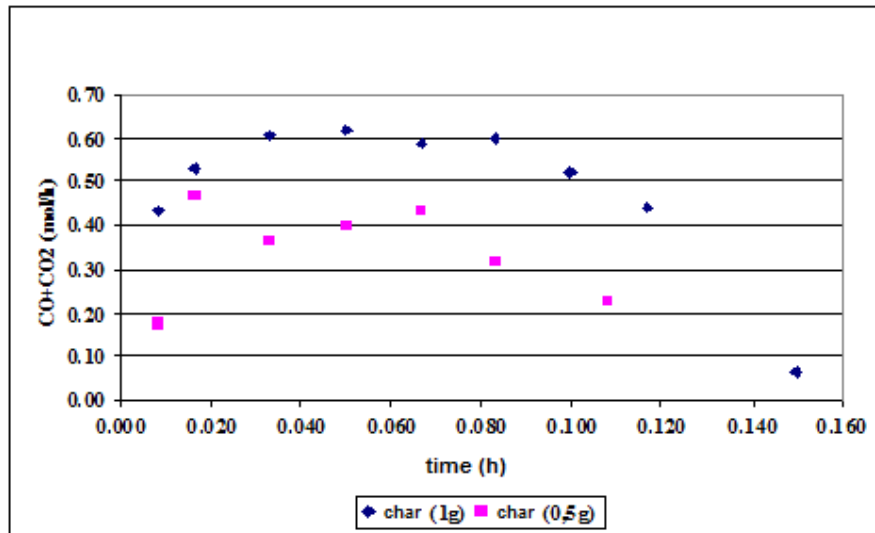

Fig. 3. The influence of char mass on the gasification period:
pyrolysis at 450°C for 15 min, gasification at 1000°C, 1gH2O/min.

The difference of position that represents the different quantities of gas proportional to different content of fixed carbon (content that doubles from 0.5 g to 1g of char) generates different molar quantities of CO+CO2.

Influence of pyrolysis temperature and residence time

For this study we chose as sample the wood due to easy manipulation and sampling. To establish a clear influence of this parameter we chose the maximum possible difference of temperature for two pyrolysis process with similar devolatilisation kinetics 600°C and 950°C. The mass reduction presented in figure 4. is calculated as function of CO and CO2 formation during our experiments.
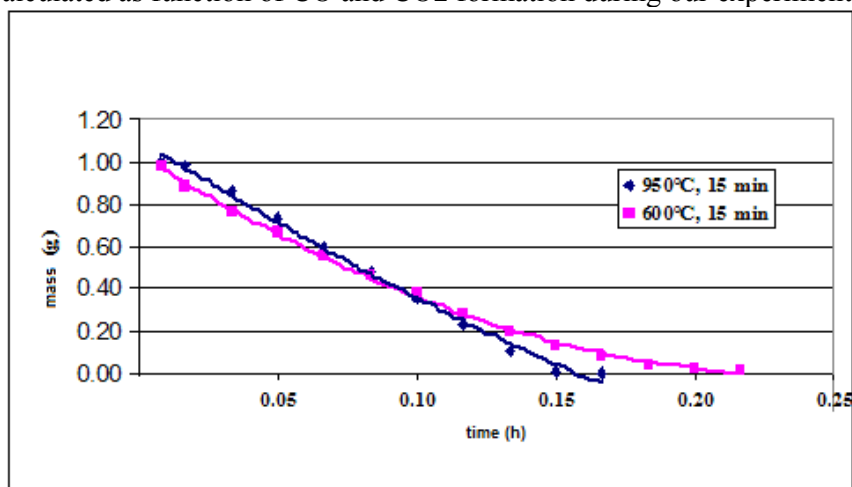

Fig. 4. The wood char mass variation during atmospheric steam gasification for different pyrolysis temperatures (pyrolysis residence time = 15 min), gasification 1000°C, 1.15 g_{H2O}/min

Diagram 4 shows a faster mass variation for the wood char obtained at a higher temperature pyrolysis. The process ends after about 10 minutes compared to 14 minutes required by char from 600°C pyrolysis. The pyrolysis temperature increase from 600° to 950°C reduces the residence time required for a complete gasification of the char with approximately 29%. That can be explained by the more fragile structure of the char obtained at elevated temperatures due to higher heating rate. The rapid temperature increase involves an augmentation of char porosity and a higher specific surface. Consequently the contact surface between the char and the gasification agent will increase, reducing the reaction time.

A series of experiments were performed using two types of wood char: from pyrolysis at 450°C after 15 and 45 minutes residence time.

Figure 5. shows the same evolution for sample mass reduction rate meaning that reactions period are similar proving the independence of gasification kinetic of pyrolysis residence time. Therefore we can conclude that pyrolysis

treatment period conducted at low temperature does not influence the vapour-gasification kinetics or carbon based gaseous species formation.
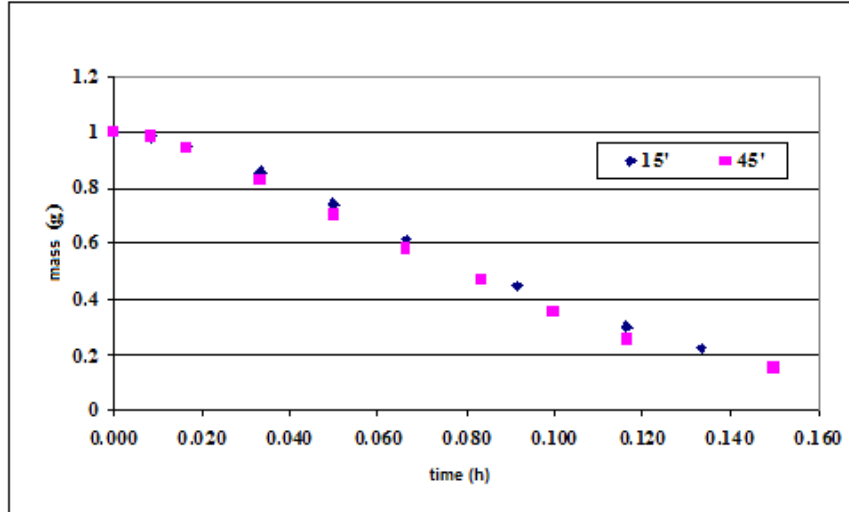

Fig. 5. Wood char mass reduction rate under vapo-gasification condition as function of pyrolysis treatment period at 450°C (15 min / 45 min), gasification 1000°C, 1 g_{H2O}/min

For experiment validation we made a series of tests to check the influence of pyrolysis treatment period on the gasification kinetics for 600°C that corresponds to moderate temperature pyrolysis (figure 6).
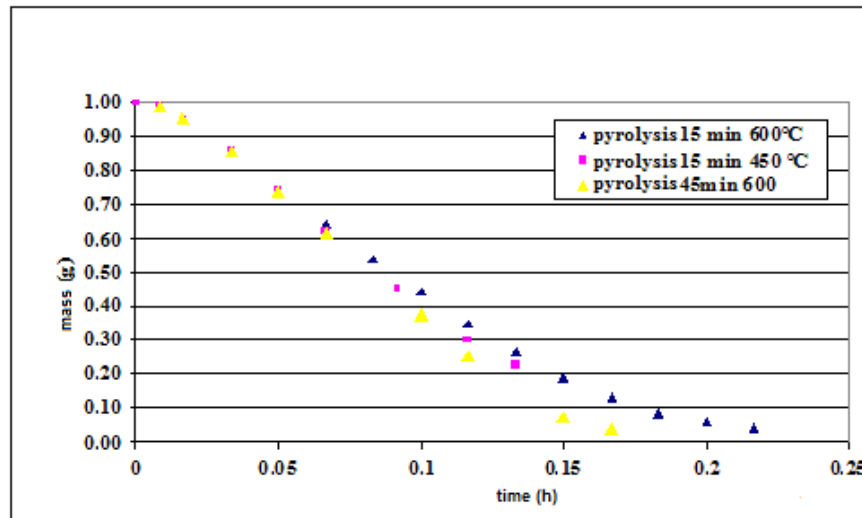

Fig. 6. Wood char mass variation under vapour-gasification conditions as function of pyrolysis treatment period and temperature (moderate), gasification 1000°C, 1 gH2O/min

There is a slight effect of pyrolysis residence time for temperatures above 600°C – 650°C on the gasified char mass variation. This could be explained by one mechanism that takes place under pyrolysis conditions starting with 600°C: the $CaCO_3$ liberation. Above this temperature level starts the decomposition of calcium carbonate and the wood char becomes more porous. The reaction is rather slow; therefore longer the pyrolysis treatment period is more carbonate is liberated. It is very well known that $CaCO_3$ is present especially in cellulose compounds, and for plastic compounds this mechanism is not valid.

4. Conclusions

With respect to char nature we noticed that the required period for the complete gasification of the wood char is about 9 min, compared to plastic 15 min. The char structure strongly influences the process kinetics. The products based on plastic require a residence time with about 66% longer than the cellulose based products. For the mixtures, the product with the slowest kinetic imposes the residence time. Regarding the pyrolysis temperature influence on the gasification kinetics the experiments showed a faster mass variation for the wood char obtained at a higher temperature pyrolysis. The pyrolysis temperature increase from 600° to 950°C reduces the residence time required for a complete gasification of the char with approximately 29%. Therefore we can conclude that pyrolysis treatment period conducted at low temperature does not influence the vapour-gasification kinetics or carbon based gaseous species formation. For pyrolysis temperatures above 600°C – 650°C there is a slight effect of pyrolysis residence time on the gasified char mass variation due to $CaCO_3$ presence in the char. The variation of char mass under gasification conditions was calculated based on CO and CO_2 mass fraction measured in the syngas.

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