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From biomass towards syngas

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Abstract

The article presents and overview of selected physical and chemical issues relating to biomass gasification. It also includes the history of the development of thermal wood treatment technology, with particular attention paid to Polish threads. Basic physical and chemical properties of biomass are discussed, using wood and straw as representative examples. Main types of gravitational gasifying reactors are presented, along with the analysis of basic mechanisms of homogeneous and heterogeneous chemical reactions in the reactor bed. The equation of motion of bed particles is derived based on particle volume changes caused by pyrolysis and surface reactions.

Keywords: Biomass; Pyrolysis, Gasification; Bed subsidance, Reactions

1 Introduction

Wood gasification is not a new technology. Archaeological research has revealed that its version consisting in wood carbonisation was already known as early as several thousand years ago. A basic goal of the wood carbonisation technology was to produce charcoal, which until the nineteenth century was the main raw material for various economy sectors. Charcoal was used in smelters and forges, as its high combustion temperature, above 2000 °C, by far exceeded the melting point of iron, which is slightly higher than 1100 °C. Charcoal was also used in medicine and gunpowder production.

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The applications believed to be most important from among all charcoal application areas referred to smelting and working of iron, i.e. the material which, due to its importance to the economy and the scale of use, required continuous and continually growing production.

Polish literature concerning charcoal production is interesting and surprisingly reach. Presumably, the first text in Polish which described wood carbonisation is, to our surprise, the poetic work written by Walenty Roździeński in 1612 and entitled *Officina ferraria albo huta y warstat z kuźniami szlachetnego dzieła żelaznego* (“Officina ferraria or smelter and workshop with noble iron matter forges”) [22]. This work is of particular importance in the context of the history of wood gasification, as one Chapter, entitled *Węgielnicy* (“Coal workers”) presents principles of charcoal production. Roździeński draws attention to major factors affecting charcoal quality, such as: adequate size of wood and its dryness, and tightness of the charcoal pile sand cover. According to the over 400 years old description, an important factor for good carbonisation is the rate of wood combustion, which is to be moderate – “niechaj raczej powoli z nienagła idzie” (“should go rather slowly, and not rapidly”).

In 1650, Kazimierz Siemienowicz [23], an artillery engineer, published a manual on artillery entitled *Artis Magnae Artilleriae pars prima*. This book, very popular in Europe in the 17th and 18th centuries, includes a brief section concerning charcoal production. Its description is concise and presents recommendations on how to select wood and lay it down inside the charcoal pile. The next text dealing with wood carbonisation appears in the context of iron production. Father J. Osiński, a Piarist, in the book published in 1782 and entitled *Polskich żelaza fabryk opisanie* (“Description of Polish ironworks”) [13] writes about dimensions of charcoal piles and outputs of charcoal production based on different types of wood.

The first publication in Polish literature which was fully devoted to wood carbonisation was the book written by Alojzy Szwęska and entitled *Sztuka węglenia drzewa doświadczeniem stwierdzona* (“Experimentally proved wood carbonisation art”) [24]. The book describes the state of technology at that time. Szwęska proposes solutions to certain problems and questions concerning, for instance, selecting the time of year for felling trees and wood carbonisation, and best types of wood for these purposes. Being a general forest supervisor in Galicia, then under foreign occupation, he formulated principles of charcoal pile construction, including their shapes and cladding methods. He recommended vertical wood piling as bringing lower losses.

He wrote that although the time of carbonisation depends on many factors, such as: the size of the pile (the volume of which can range from 80 to 120 m³), the type and size of wood, and the permeability of cladding, the entire process lasts, in general, not longer than 20 days after firing the pile. Evaluating the quality of the produced coal consist in evaluating its fragility – less fragile coals represent higher quality, density – heavier coals are better, and the sound emitted during coal breaking. Finally Szweńska admits that it is personal experience of a coal producer which counts most. In those times good charcoal was already used for heating houses, but compared to wood, it was definitely less popular as a fuel due to its high price. Szweńska rightly pointed out that the density of charcoal is 5 times as low as the density of wood, while its calorific value is only slightly lower.

A little later, in 1820, A. Dunin described in *Sylwan* [4], a journal which is published to this date, a methods of charcoal production. This publication discussed energy efficient technology of carbon smouldering making use of modern charcoal kilns. Those kilns, which replaced traditional piles, should have double walls separated by an athermal air partition. Thermal savings in this case can amount to about 15%. In his publication Dunin also analysed chemical reactions taking place during combustion and gasification, presented the wood composition, introduced the term of “cieplik” (caloric), and described the course of combustion and gasification processes.

A very important publication describing the development of technology of wood carbonisation was the book entitled *O suchej destylacji drewna* (“About dry wood distillation”) by Edmund Weżyk [29]. This was a technical and scientific publication, full of technological details and pieces of information on chemical compounds recorded in the process. Its high level of modernity for that time is best testified by the fact that 50 years later this book was still used to describe the carbonisation process [21]. The book by Weżyk includes carefully made woodcuts (Fig. 1) which present various types of charcoal piles and kilns. Unlike the publications by Dunin and Szweńska, its chemical language does not differ much from that presently used.

Certain inventions became milestones in the development of the solid fuel gasification technology. The earliest experiments concerned gas production from coal. In 1659 Thomas Shirley obtained experimentally gas from hard coal, while in 1699 Dean Clayton produced the pyrolytic gas from coal [2]. Enormous progress in practical use of coal was observed in the United Kingdom in the 18th and 19th centuries. Along with its combustion

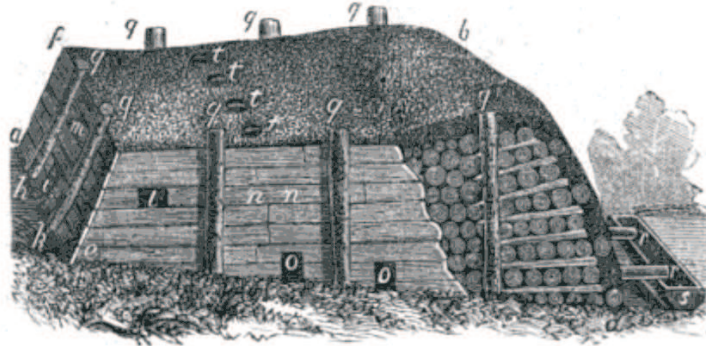


Figure 1: Woodcut of charcoal pile from [29].

in steam engines, English and Scottish engineers developed the technology of coal gasification. When talking about prominent figures for the development of this technology, persons who are worth mentioning here are: Robert Gardner, who obtained a patent for coal gasification in 1788, and Murdock, who popularised the use of gas for heating and illuminating purposes on British Islands. At the end of the 18th century, a device which made use of gas obtained in wood carbonisation for illumination and heating purposes was patented by Filip Lebon, a French engineer.

In the second part of the 19th century an internal combustion engine was invented. This invention had a huge impact of the development of civilisation. The first piston engine, patented by E. Lenoir in 1860, was gas fuelled, while the petrol engines constructed by Benz and diesel engines constructed by Diesel appeared later. It is noteworthy that the Lenoir engine was fed with the mixture of city gas and air. Despite its low power, it is recognised now as the first well functioning internal combustion engine. The Otto engine was also gas fuelled.

Wood gasification turned out to be an important technology of engine fuelling during the Second World War. In that time, the shortage of fuels forced many countries to build generators of wood gas, used then as a fuel in internal combustion engines. This situation had place in Sweden, Germany, and the United Kingdom, where large numbers of wood gas powered vehicles appeared on the roads. Of particular importance was the year 1944 in which the Allies began a bombing offensive with an aim to destroy German petroleum industry, including refineries, chemical plants, and synthetic fuel

production plants. Just after the end of the Second World War, tractors in Ukraine were commonly fed with syngas. Low prices of crude oil were the reason why until 1970s petrol was unbeatable as the fuel. The 1970s, in turn, brought the military conflict between Israel on the one side, and Egypt and Syria on the other side. As a result of military assistance provided by the United States to Israel, on 20 October, 1973, the Arab OPEC countries led by Saudi Arabia put an embargo on crude oil shipment to the USA, and then to Western Europe countries. All this has led to the oil crisis which impacted the world economy and gave a strong impulse for development of alternative technologies, such as gas production from biomass and coal.

2 Physical properties of fuels

Biomass encompasses a wide variety of raw materials formed as a result of photosynthesis. In economic aspects, two types of biomass, namely wood and straw, are of highest importance. In Poland, up to 7 million m³ of wood is used per year for energy conversion, which corresponds, in weight terms, to about 3.5 million tonnes. Straw production in Poland amounts to over 10 million tonnes per year, out of which about 3 million tonnes remain available for energy conversion. This is a meaningful source of fuel, which may affect the power balance of the entire country.

Wood is a porous material, and its physical properties depend on the place from which the sample is taken. Moreover, it reveals anisotropic structure, which affects its mechanical strength and thermal properties. Straw, consisting of similar chemical compounds as wood, additionally reveals low density and very high porosity.

Wood and straw are materials revealing relatively low mass density, low thermal conductivity, and high mechanical strength. The material compound which decides about their mechanical properties is cellulose. Walls of biomass cells, built of cellulose microfibrils, are capable of carrying high loads. Tensile strength tests of a single wood cellulose fibre return the value of 164 MPa [12], which is comparable to that revealed by carbon steel.

The nonuniform structure of wood can be seen in the photo taken using an optical microscope (Fig. 2). The photo shows radially arranged grains, formed as a result of wood mass increase during its growing.

Wood has not only non-uniform, but also porous structure. It consists of different tissues, the most important of which are wood fibres, vessels, and

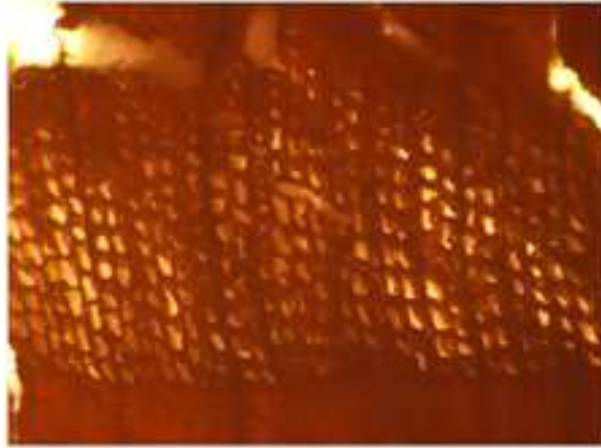


Figure 2: Cross section of pine wood viewed under optical microscope [8].

quills, depending on the type of wood. All these elements have elongated shapes and are empty inside – this empty space can be occupied by water. Wood fibres, which are the basis of the structure of deciduous woods, have circular or polygonal cross sections. Their length ranges from 0.7 mm to 1.8 mm, while the diameter can change from 0.02 mm to 0.05 mm. The length-to-diameter ratio can amount to about 35. Another type of deciduous wood tissues are vessels. They have cylindrical shapes, with the length ranging between 0.2 mm and 1.3 mm and the diameter from 0.03 mm to 0.5 mm. The length-to-diameter ratio for vessels is smaller than that for fibres, and ranges between 2.6 and 7.

Quills are basic cells of coniferous trees. They have a spindly shape, and their cross section is a quadrangle having the side dimension from 0.02 mm to 0.07 mm. The length of a quill varies from 2 mm up to 10 mm, which gives the length-to-diameter ratio from 100 to 140.

The straw structure differs from that of wood, see Fig. 3. Thin walls of straw are built of tubes, a structure which ensures mechanical strength. The emptiness of the inner space is the reason why the material density is low.

A remarkable difference between the wood and the straw consists in high density disproportion between both materials. The density of wood mainly depends on the type of wood, place of origin, weather conditions, humidity, and wood section from which the sample is taken. Leaving aside material porosity, the wood substance itself has relatively high density ranging from

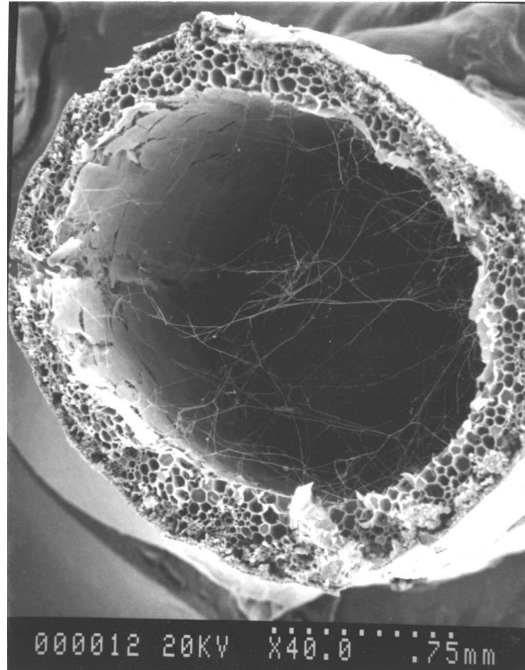


Figure 3: Photo of the cross section of straw [16].

1500 kg/m³ to 1564 kg/m³. The density range of the wood is relatively wide, from 470 kg/m³ to about 760 kg/m³. Table 1 collects densities of selected species of wood in the analytical state.

Table 1: Density of selected species of wood in dry air conditions [20].

Wood	Density of mass, kg/m ³	Wood	Density of mass, kg/m ³
Oak	760	Larch	590
Hornbeam	740	Alder	540
Beech	710	Pine	520
Maple	690	Fir	470

The density of loose straw is ten times as low as that of wood and ranges between 40 and 60 kg/m³, reaching up to 150 kg/m³ in case of heavily compacted straw. The difference in density is very large, although the

contents of carbon and hydrogen in wood and straw are similar, see Tab. 2. Wood and straw differ by oxygen content, which is lower by 7% in straw than in wood.

Table 2: Elemental composition of wood and straw [3,8].

Mass fraction, %	Biomass	
	Wood	Straw
C	46.2	44.9
H	6.0	5.9
O	47.7	37.6
N	0.1	0.7
Cl		1.5

Technical analyses reveal that the straw contains much more fix carbon and ash than the wood (Tab. 3). Relatively large amounts of ash force the use of different methods for ash disposal in straw gasification and combustion installations.

Table 3: Technical analysis of wood and straw [3], [8].

Mass fraction, %	Biomass	
	Wood	Straw
Fix carbon	18.1	30.6
Volatile components	80.2	69.4
Ash	1.7	10.6
Combustion heat MJ/kg	18.6	17.7

Substantial differences can also be observed in chemical composition of these two materials. The dominating wood component is cellulose, while in straw it is hemicellulose (Tab. 4). The amount of hemicellulose in straw is twice as large as in wood.

3 Types of reactors with porous beds

High capacity solid fuel gasification installations make use of flow reactors in which the fuel is crushed to very small size to react better and faster

Table 4: Chemical composition of wood and straw [3,8].

Mass fraction, %	Biomass	
	Wood	Straw
Cellulose	49.8	28.8
Hemicellulose	20.7	39.4
Lignin	27.0	18.6

with the oxidant. Reactors with fluidised bed are also in use. Due to their sizes, both flow and fluidised reactors are expensive in the investment phase, therefore their use in small installations is not economically justified. Low power reactors, discussed further in the article, make use of fuel crushed to a few centimetres to compose a porous bed. Low power reactors with porous bed can be basically divided into cocurrent, countercurrent and crosscurrent installations.

In cocurrent reactors the fuel charge and the gasifying medium move in the same direction – downwards in the reactor (Fig. 4a). The fuel entering the reactor undergoes drying and pyrolysis, and finally is gasified at the presence of the gasifying medium. The top layer of the fuel contains wet fuel through which the air flows. The next layer is involved in the process of pyrolysis in which volatile components are released from the preliminarily dried biomass. Below this layer, most of the pyrolytic gases are combusted, thus delivering heat to the upper layer in which the process of pyrolysis has place. In the lowest part of the reactor the reduction processes take place in which the created charcoal reacts at high temperature with the exhaust gas. If the time of gas residence in the gasification zone is too short, or the temperature is too low, this may lead to gas condensation to tar and tarry substances in the reactor. The syngas temperature at the cocurrent reactor exit exceeds 500 °C [11]. The structure of the reactor requires uniform distribution of fuel charge in the bed. Gas products of this reactor reveal low content of tarry substances, which allows relatively pure gas to be obtained.

In countercurrent reactors, (Fig. 4b), the fuel is inserted to the reactor from top and then moves downwards while the gasifying medium flows in the opposite direction. The descending fuel undergoes drying and gasification stages, finally being involved in the reduction process taking place in the biochar bed and the combustion process. As compared to the cocurrent

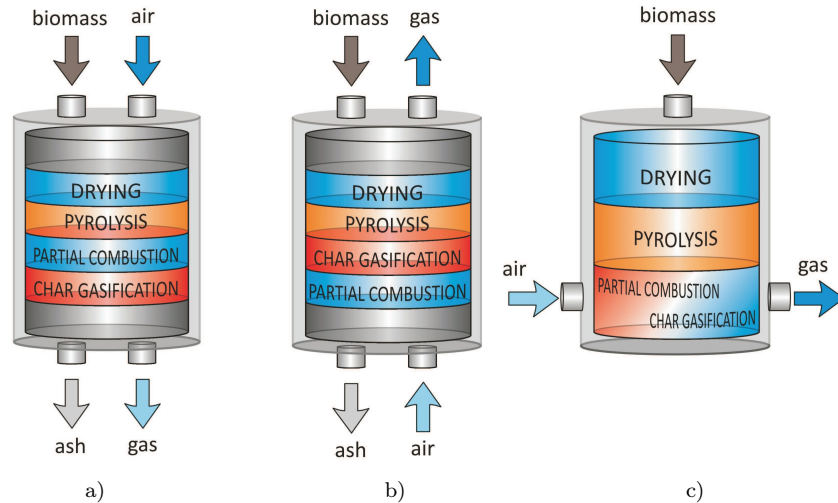


Figure 4: Types of reactors which gasify solid fuel in porous bed a) cocurrent, b) counter-current, c) crosscurrent [11].

reactor, here the gas flowing through the dried biomass reveals low content of dust and high content of tar. At the same time the process itself reveals high thermal efficiency. Moreover, the gas flowing through the biomass bed contributes to its well drying, thus providing opportunities to use fuel charges of relatively high humidity.

In the crosscurrent reactor (Fig. 4c) the fuel is inserted to the reactor from top, while the gasifying medium is delivered via a nozzle situated on a side of the reactor, above the grate. The charge moves, consecutively, through the drying and pyrolysis zones, and finally through the volatile compound oxidation and reduction zones. The scheme of physical and chemical processes in the crosscurrent reactor reveals different direction than that in the remaining two types. Here, no symmetry in temperature distribution and gas composition with respect to the reactor axis is observed.

4 Pyrolysis

During biomass gasification, it is not only its mass which is subject to changes, but also its volume. Kluska [11] and Kardaś *et al.* [8] examined the pyrolysis of large elements of pine and beech wood. For this purpose photo documentation was taken, and the mass and volume of the examined elements were measured as temperature functions. The shape change of the pine cylinders is shown in Fig. 5. All examined pine cylinders had the initial volume of 6 cm^3 at the room temperature of 20°C (photo A in Fig. 5). Then the cylinders were heated in the reactor, without air access, to different temperatures: 240°C (photo B), 270°C (photo C), 320°C (photo D), 370°C (photo E), 420°C (photo F), 470°C (photo G) and finally 520°C (photo H). After each experiment, photos of the selected samples were taken, see: the next photos in Fig. 5 presenting differences in sizes and shapes between particular wood samples. Up to the temperature of 370°C cylinders shrank, while in higher temperatures, of 420°C and 470°C , their volume increased. At the highest temperature of 520°C the volume decrease of the examined samples was observed again.

The mass change of the examined wood is a function of the temperature in which the pyrolysis was conducted and the rate of heating of the sample. Volumetric changes taking place during wood heating without oxygen access depend not only on the above parameters, but also of the size of the sample and way of its crushing. The volume increase can be explained as the result of the increase of the inner pressure during pyrolysis, caused by intensive gas emission [17]. The effect of swelling of wooden cylinders in the pyrolysis process was examined by Pattanotai *et al.* [18,19] Kluska [11] examined changes of mass and volume of beech cylinders. The results of mass measurements of beech wood samples reveal the same nature as for pine wood – their mass decreased with the increasing temperature (Fig. 6). However, the volume of the beech cylinders changed in another way than in case of pine samples – it decreased monotonically with the increasing temperature (Fig. 6).

The recorded temperature dependent mass losses show that the highest loss took place within the temperature range of $240\text{--}320^\circ\text{C}$. The final mass amounted to 23% of the initial mass, which is consistent with the results of thermogravimetric analyses. The final volume decreased to 37% of the initial volume, and the density of the beech wood decreased from 0.75 g/cm^3 to 0.47 g/cm^3 .

When heating the biomass which mainly consists of cellulose, hemicel-

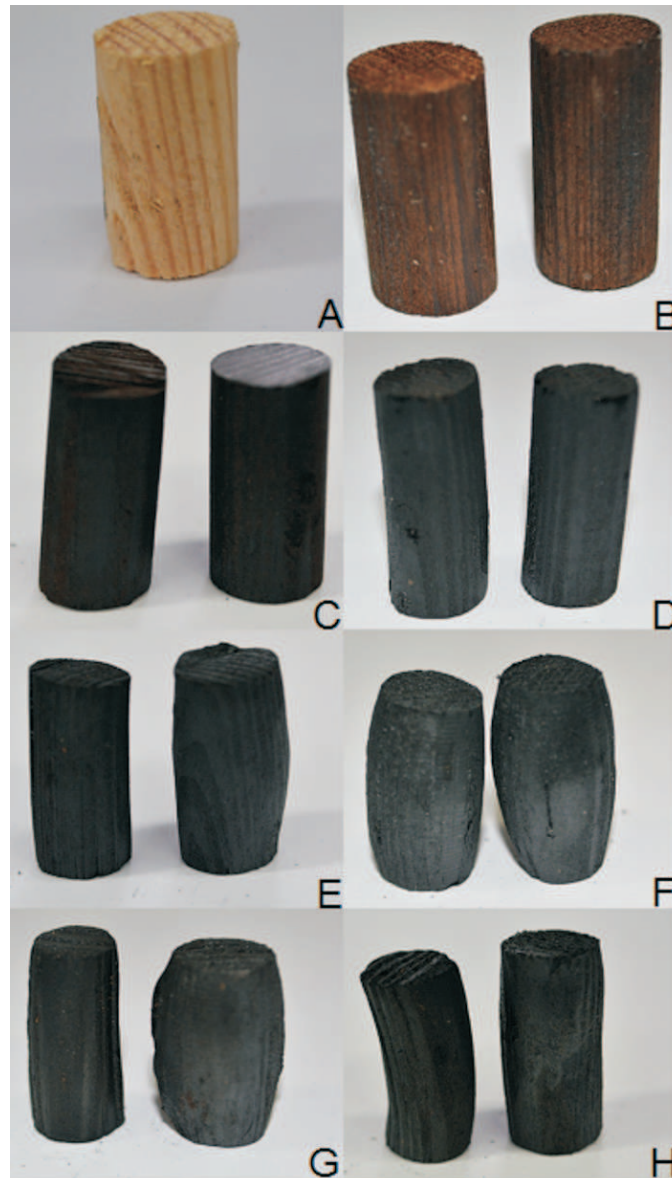


Figure 5: Photos of pine cylinders heated to different temperatures in the pyrolysis process [8].

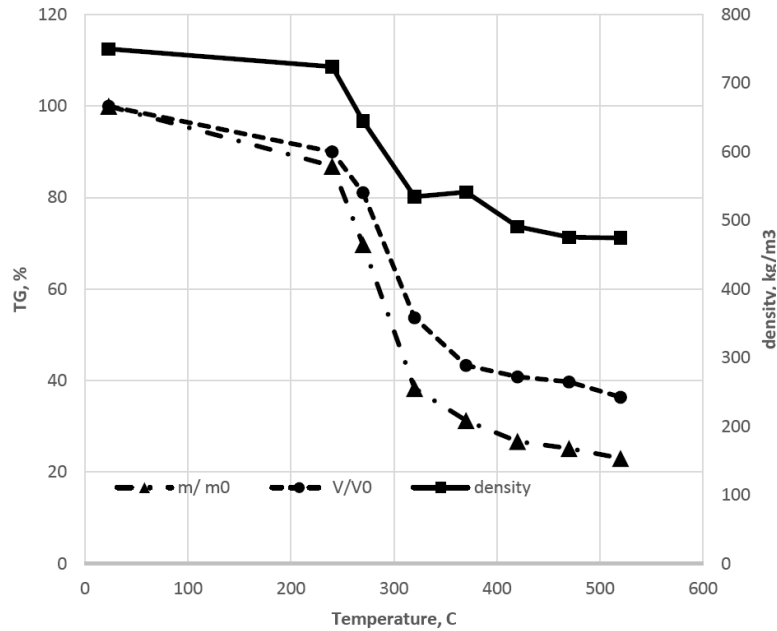


Figure 6: Relative volume, mass and mass density of pine cylinders vs. pyrolysis temperature [11].

lulose and lignin, the solid phase is subject to decomposition. This process depends, most of all, on the chemical composition of the charge and the temperature, but also on the rate of heating, the biomass structure, and the level of crushing. The course of cellulose, hemicellulose and lignin pyrolysis is shown in Fig. 7 [28], presenting mass changes of particular components resulting from temperature changes. The course of pyrolysis is different for each biomass component. Cellulose decomposes at temperatures from 300 °C to 400 °C, while hemicellulose decomposes earlier, from 200 °C to about 400 °C. Due to its nonuniform composition, the pyrolysis of lignin takes place within a very wide temperature range, from 200 °C to 500 °C.

During pyrolysis, part of biomass converts into a mixture of gases, the composition of which depends on the temperature. The examinations carried out by Kluska [11], and Kardaś *et al.* [8], have documented changes of particular fractions of basic gas products obtained in the wood pyrolysis. These results agree in qualitative terms with those obtained by Fagbemi [5], Zollezi [31], Amutio [1] and Li [16].

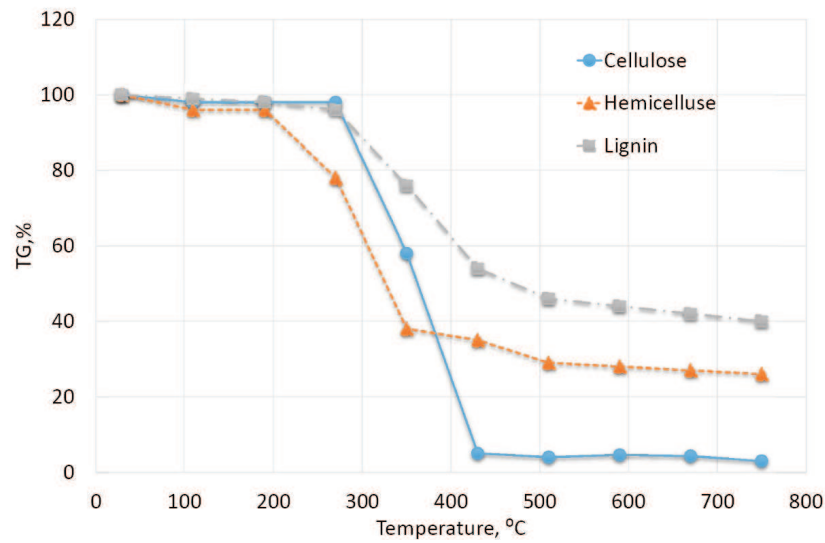


Figure 7: Thermogravimetric diagrams of mass change vs. temperature: for cellulose, hemicellulose, and lignin [28].

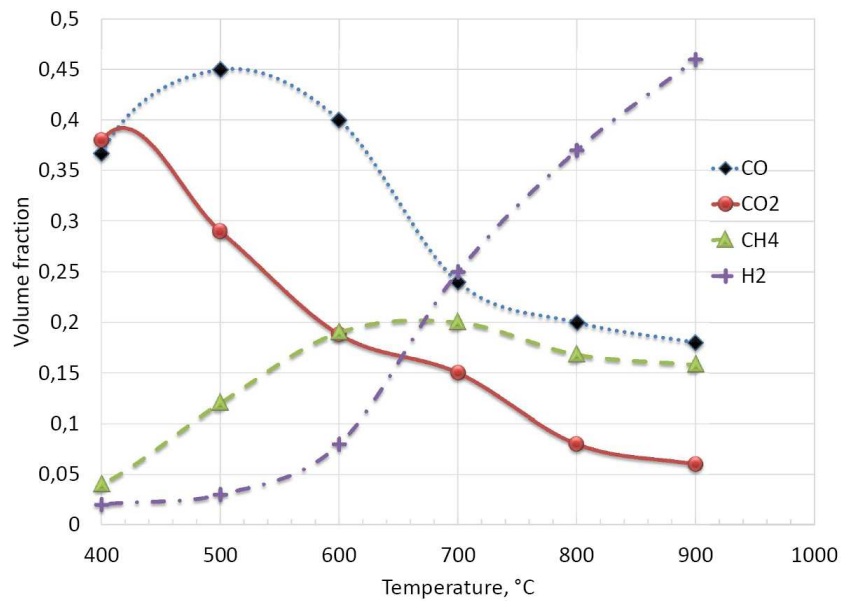


Figure 8: Volume fractions of gas products obtained in wood pyrolysis vs. temperature.

Figure 8 shows volume fractions of basic gas products obtained in the wood pyrolysis as temperature functions. CO_2 , CO , CH_4 , and H_2 are the components with the highest volume fractions in the pyrolytic gas. The CO_2 fraction is the highest at the temperature of 400°C and then decreases, while the CO fraction reaches the maximum of 45% at the temperature of 500°C and decreases below 20% at temperatures exceeding 800°C . The only gas whose fraction increases with temperature is H_2 . It is noteworthy, however, that the portion of the pyrolytic gas produced at high temperatures is very small – the overwhelming majority of the gas is produced at temperatures within 300°C to 500°C .

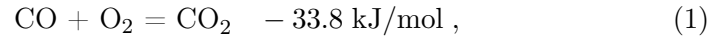
5 Chemical reactions

Biomass decomposition during the pyrolysis is the first phase of chemical reactions composing the gasification process. The next two stages include oxidation and reduction reactions. The oxidation reactions take place, most of all, between the pyrolytic gases and the air, and are of homogeneous type. Depending on the air volume, fuel oxidation processes with biochar can also take place on surfaces (heterogeneous reactions). In case of full pyrolysis of volatile components, the formed gas contains all oxygen and hydrogen from the fuel and the remaining part of carbon C. The biochar consists of carbon and ash. Assuming that the elemental composition of wood is that given in Tab. 2 and taking into account the data from Tab. 3, the proportion of fractions of carbon C, hydrogen H, and oxygen O in the pyrolytic gas is as 36:7:57. As can be noticed, it is oxygen which is the dominating chemical element in the pyrolytic gas. The biochar, in turn, consists of 91% carbon and of 9% ash. Combustion of the gas products of the pyrolysis depends on what gases have been created in the pyrolysis zone. Along with the above named gas products, the pyrolytic gases also comprise a series of condensing compounds having the form of a mixture of tar and water. The amount of liquid products of wood pyrolysis [8] which have been obtained in a large number of tests range between 37% and 48%. At high temperatures the tar is a mixture of volatile substances which can also take part in oxidation.

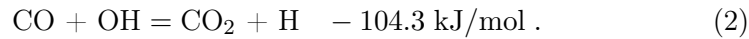
5.1 Carbon monoxide

The reactants of pyrolytic gas combustion are the already mentioned CO , CO_2 , CH_4 and H_2 . But in fact, the mixture of gases in the gasifying reactor

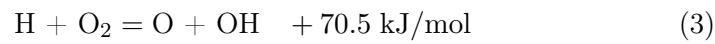
contains much more chemical compounds and free radicals. Of high importance for gas combustion reactions are the OH groups, and free O and H radicals. This situation can be observed when combusting carbon monoxide. The reaction of direct oxidation of CO, the basic syngas component, looks simple in a written form



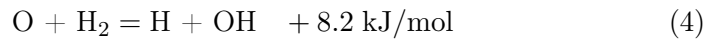
but is unlikely, due to high activation energy, equal to 201 kJ/mol [15]. The situation changes after introducing a small amount of hydrogen, as in this case the OH group reacts directly with the carbon monoxide molecule, according to the formula [25]



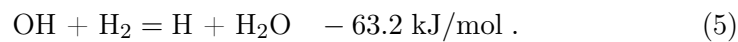
This type of reaction dominates in the process of carbon dioxide, CO₂, formation, provided that it takes place in the presence of OH groups. The OH group can be created as a result of the reaction of a free H radical released in the reaction (2) with oxygen



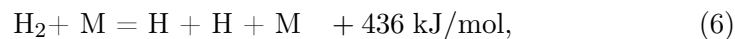
or in the reaction



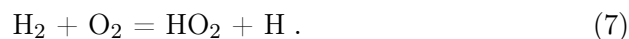
followed by the reaction



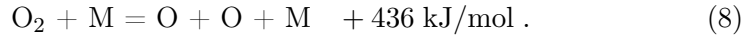
The reactants in the reactions (3)-(5) are: oxygen, which is an air component, and the above mentioned hydrogen. Along with the already mentioned reactions (2), (4) and (5), free H radicals are created in other reactions, including the reaction of molecular hydrogen dissociation (Turns, 1996)



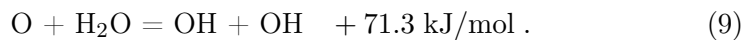
and the reaction between hydrogen and oxygen



The free O radical, in turn, which takes part in the reaction (4) leading to the formation of the OH groups (Turns, 1996), is created as a result of the molecular oxygen dissociation



Free oxygen radicals are of high importance in CO combustion in the presence of steam. In this case not only hydrogen but also steam can be a catalyser of the CO combustion process. This situation has place when free O radicals from the reaction (8) react with water according to the formula

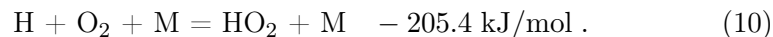


The OH group formed as a result of this reaction becomes the reactant in the reaction (2).

5.2 Hydrogen

Hydrogen is important in pyrolytic gas combustion processes, as it is the second combustible component of the mixture, after carbon monoxide. The course of hydrogen combustion highly depends on pressure and temperature. A condition for hydrogen combustion is the presence of free radicals. In the hydrogen-oxygen relation, free radicals are created in endothermic reactions (6), (7), and (8). The activation energy for the reaction (8) is the lowest, therefore this type of reaction is most likely. At higher temperatures, the presence of hydrogen dissociation fraction (6) becomes more important. The oxygen dissociation reaction (7) is less likely because the binding energy of the oxygen molecule is higher than that of hydrogen. Formation of free H radicals provides opportunities for hydrogen combustion. The process starts from one of the three reactions (3), (4), or (5) [14]. None of these reactions has a dominating effect on the course of hydrogen combustion, but they play an important role in increasing the number of free radicals. The reactions (3) and (4) are rare, as they involve free H and O radicals, and the number of these radicals is small.

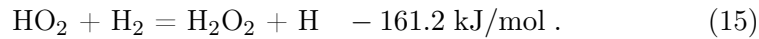
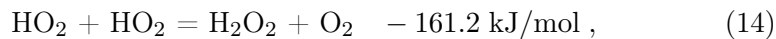
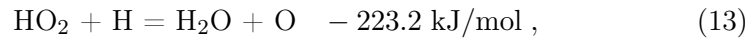
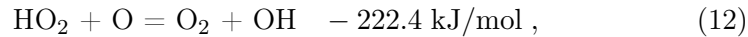
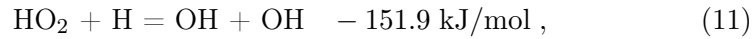
The pressure increase changes the relations between oxygen and hydrogen, and the reaction (3) becomes less important than the reaction involving high energy molecules, which leads to the formation of free HO₂ radical



The created free HO₂ radical is not very reactive, and therefore can survive collisions with other molecules and with the reactor walls. The reaction (10)

decreases the rate of the hydrogen combustion reaction.

Further pressure increase leads to higher HO₂ concentration. As a consequence, the following reactions gain in importance

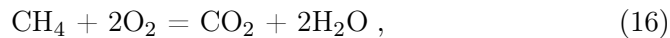


Depending on the temperature, the mixture of oxygen and hydrogen can become explosive. At the temperatures exceeding 600 °C, oxygen and hydrogen compose the explosive mixture within the entire range of possible pressures. At lower temperatures (400–580 °C), the rate of hydrogen combustion changes. The explosiveness limit forms a Z shaped curve in the pressure-temperature diagram [14].

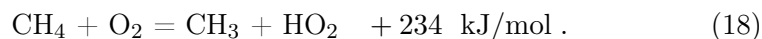
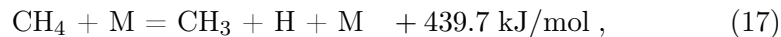
5.3 Methane

In fraction terms, methane is the third component of the pyrolytic gas mixture. Since it is a basic component of the natural gas, studies of methane combustion kinetics are very intensively developed. For instance, Kaufman claims that during one decade the number of formulas used to describe the combustion mechanism increased from about ten basic reactions to 75 [10]. A slightly later publication by Frenklach *et. al.* [6] already says about 144 elementary reactions.

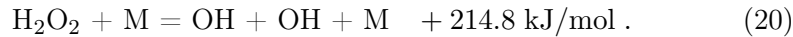
The global reaction of methane combustion has the following form:



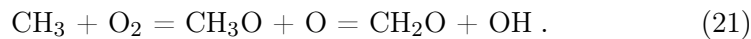
but in fact it consists in a series of complicated elementary reactions. According to Glassman [7] and Law [14], methane combustion starts from one of the following two reactions:



Since it requires very high activation energy, the former reaction dominates at high temperatures. When the temperatures are lower, the reaction (18) gains in importance, after which the following reactions take place:



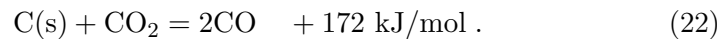
At the next stage, free radicals react with molecular oxygen



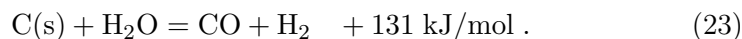
Thus, the direction of the combustion reaction is the following: firstly the hydrogen fraction is reduced from CH_4 to CH_3 and CH_3O , then to CH_2O and HCO , and finally to CO . The reaction of CO combustion was discussed earlier in this Section, and what is only noteworthy here is that of key importance for its course is the OH group concentration.

5.4 Char combustion

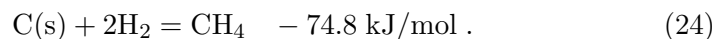
Surface reactions with charcoal are very complex, as they depend not only on thermodynamic parameters of the substrates but also on the structure of the fuel. Basic agents which react with charcoal are: oxygen, carbon dioxide, water, and hydrogen. At the absence of oxygen, the reactions which have place on the bed of heated biochar involve gas products of pyrolysis and carbon. The CO_2 reaction with charcoal, bearing the name of the Boudouard reaction, leads to the production of carbon monoxide



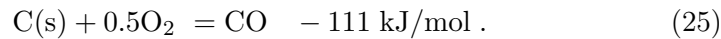
This reaction affects significantly the composition of the syngas. Its significance increases with the increasing temperature, especially above 1000°C when the reaction rate is higher and CO_2 reduction becomes remarkable. Carbon reduction with steam (water-gas reaction) produces syngas, i.e. the mixture of carbon monoxide and hydrogen



The hydrogen contained in the pyrolytic gas, or that created in (23) as a result of the reaction with carbon (methanisation), takes part in production of methane

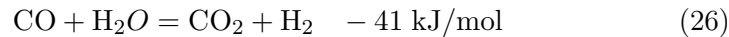


A situation can have place during gasification when oxygen molecules react with charcoal. This situation can be observed, for instance, in the vicinity of the air inlet. Exothermic reaction of carbon oxidation leads to production of CO

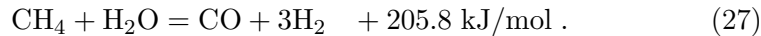


The above reactions occur at different rates, depending on the activity of the gasifying agent. The most active agent is oxygen, consequently the fastest reaction is (25) which absorbs all available oxygen. The carbon-steam reaction (23) is three to five orders of magnitude as slow as the reaction with oxygen (25). And the Boudouard reaction is even slower and its rate, compared to the reaction (25), is 6–7 times as low. The slowest reaction is the hydrogen-carbon reaction (24). According to Walker *et al.* [27] the relative rates, R , of these reactions at temperature of 800 °C and under pressure of 10 kPa are equal to: $R_{\text{C}+\text{O}_2} \approx 10^5$, $R_{\text{C}+\text{H}_2\text{O}} \approx 10^3$, $R_{\text{C}+\text{CO}_2} \approx 10^1$, $R_{\text{C}+\text{H}_2} \approx 10^{-3}$.

Under the assumption that the entire carbon takes part in conversion, subtracting the Boudouard equation from that describing the carbon-steam reaction gives



while subtracting the equation describing the methanisation reaction from that describing the carbon-steam reaction leads to



Equations (26) and (27) represent the equilibrium between CO, H₂O, CO₂, H₂, and CH₄.

The result of the surface reactions depends on thermodynamic parameters of gas substrates: temperature and concentration, but also on the time of process duration. This latter quantity depends, in turn, on the speed of fuel motion.

6 Bed motion – subsidence

The bed packed in the gravitational gasifying reactor moves down due to the action of the gravitational force and the pressure exerted by higher layers on lower layers in the bed. For the packed bed, the motion of particles is accompanied with the loss of their volume. The starting point for deriving

The below presented analysis aims at deriving the equation of motion in Eulerian coordinates for solid phase particles which move through the porous bed revealing the above described properties. The analysed system consists of the same particles (but not having the same volume and mass) at two successive close time steps. At the initial time step, t_1 , the system occupies the volume V_{p1} , then starts moving and at the final time step $t_2 = t_1 + \Delta t$ it occupies another volume V_{p2} . The velocity of motion of the particles in the volume is denoted as $\vec{v}(r, t)$, and the normal vector to the moving surface is \vec{n} . The fixed control volume V_k is limited by the surface A_k , which consists of two parts: A_a and A_b . The equation of motion of solid phase particles in the control volume V_k will be derived from an equation formulated for the moving solid phase volume V_s , which occupies part of the space V_p . Consequently we can write

$$\frac{d\varepsilon_s V_p}{dt} = -s_V \varepsilon_s V_p, \quad (29)$$

and hence

$$\frac{d}{dt} \int_{V_p} \varepsilon_s dV = \lim_{\Delta t \rightarrow 0} \frac{\int_{V_{p2}} \varepsilon_s dV - \int_{V_{p1}} \varepsilon_s dV}{\Delta t} = - \int_{V_p} s_V \varepsilon_s dV. \quad (30)$$

Since the following relations are valid between the fixed and moving control volumes:

$$V_{p1} = \varepsilon_s (V_a + V_k), \quad (31)$$

$$V_{p2} = \varepsilon_s (V_k + V_b), \quad (32)$$

then each term in Eq. (30) can be written as a sum of integrals. The first integral is

$$\int_{V_{p2}} \varepsilon_s dV = \varepsilon_s \int_{V_k} dV(t_2) + \varepsilon_s \int_{V_b} dV(t_2), \quad (33)$$

and similarly

$$\int_{V_{p1}} \varepsilon_s dV = \varepsilon_s \int_{V_a} dV(t_1) + \varepsilon_s \int_{V_k} dV(t_1). \quad (34)$$

Placing integrals (33) and (34) to Eq. (30) we get

$$\begin{aligned} \frac{d}{dt} \int_{V_p} \varepsilon_s dV &= \lim_{\Delta t \rightarrow 0} \frac{\varepsilon_s \int_{V_k} dV(t_2) + \varepsilon_s \int_{V_b} dV(t_2)}{\Delta t} \\ &\quad - \lim_{\Delta t \rightarrow 0} \frac{\varepsilon_s \int_{V_a} dV(t_1) + \varepsilon_s \int_{V_k} dV(t_1)}{\Delta t}, \end{aligned} \quad (35)$$

and after some transformations

$$\begin{aligned} \frac{d}{dt} \int_{V_p} \varepsilon_s dV &= \lim_{\Delta t \rightarrow 0} \frac{\varepsilon_s \int_{V_k} dV(t_2) - \varepsilon_s \int_{V_k} dV(t_1)}{\Delta t} + \\ &+ \lim_{\Delta t \rightarrow 0} \frac{\varepsilon_s \int_{V_b} dV(t_2) - \varepsilon_s \int_{V_a} dV(t_1)}{\Delta t} . \end{aligned} \quad (36)$$

The first right-hand term in Eq. (36) can be transformed into the partial derivative

$$\begin{aligned} \lim_{\Delta t \rightarrow 0} \frac{\varepsilon_s \int_{V_k} dV(t_2) - \varepsilon_s \int_{V_k} dV(t_1)}{\Delta t} &= \\ &= \lim_{\Delta t \rightarrow 0} \frac{\varepsilon_s V_k(t_2) - \varepsilon_s V_k(t_1)}{\Delta t} = \frac{\partial \varepsilon_s V_k}{\partial t} = 0 . \end{aligned} \quad (37)$$

The obtained result is a consequence of the adopted assumption that the volumetric fractions of particular phases do not change, and the adopted definition of the control volume which also does not change.

According to the symbols used in Fig. 8, the volume integrals V_b and V_a in Eq. (36) can be transformed into surface integrals

$$\varepsilon_s \int_{V_b} dV = \Delta t \varepsilon_s \int_{A_b} \vec{v}_{s2} \cdot \vec{n} dA , \quad (38)$$

$$\varepsilon_s \int_{V_a} dV = -\Delta t \varepsilon_s \int_{A_a} \vec{v}_{s1} \cdot \vec{n} dA . \quad (39)$$

where the velocity of motion of the solid phase volume is denoted as \vec{v}_s . Taking into account that the control volume is limited by the control surface and that this surface is the sum $A_k = A_a + A_b$, the second difference of integrals in Eq. (36) is equal to

$$\begin{aligned} \varepsilon_s \int_{V_b} dV(t_2) - \varepsilon_s \int_{V_a} dV(t_1) &= \\ &= \Delta t \varepsilon_s \int_{A_b} \vec{v}_{s2} \cdot \vec{n} dA(t_2) + \Delta t \varepsilon_s \int_{A_a} \vec{v}_{s1} \cdot \vec{n} dA(t_1) . \end{aligned} \quad (40)$$

When $\Delta t \rightarrow 0$, then the velocities $\vec{v}_{s2} \rightarrow \vec{v}_{s1} = \vec{v}_s$, and consequently

the second limit in Eq. (36) is transformed into the surface integral A_k :

$$\begin{aligned} \lim_{\Delta t \rightarrow 0} \frac{\varepsilon_s \int_{V_b} dV(t_2) - \varepsilon_s \int_{V_a} dV(t_1)}{\Delta t} &= \\ &= \lim_{\Delta t \rightarrow 0} \frac{\Delta t \varepsilon_s \int_{A_b} \vec{v}_{s2} \cdot \vec{n} dA(t_2) + \Delta t \varepsilon_s \int_{A_a} \vec{v}_{s1} \cdot \vec{n} dA(t_1)}{\Delta t} = \\ &= \varepsilon_s \int_{A_k} \vec{v}_s \cdot \vec{n} dA \end{aligned} \quad (41)$$

Placing (41) to (30) we get

$$\varepsilon_s \int_{A_k} \vec{v}_s \cdot \vec{n} dA = - \int_{V_p} s_V \varepsilon_s dV . \quad (42)$$

Applying the Gauss theorem to the surface integral we get the volume integral

$$\varepsilon_s \int_{A_k} \vec{v}_s \cdot \vec{n} dA = \varepsilon_s \int_{V_k} \text{div} \vec{v}_s dV . \quad (43)$$

When $\Delta t \rightarrow 0$ then the volume $V_p \rightarrow V_k$. As a consequence, the volume integral V_p approaches the volume integral V_k and we can write the integral equation of motion as

$$\varepsilon_s \int_{V_k} \text{div} \vec{v}_s dV = - \int_{V_k} s_V \varepsilon_s dV . \quad (44)$$

Since the control volume V_k has been assumed arbitrarily, the integral over this volume can be omitted and the equation of solid phase motion takes the form of the differential equation

$$\text{div} \vec{v}_s = -s_V . \quad (45)$$

We can see that volume changes generate the motion of the bed. The higher the rate of the volume changes, the higher the velocity of bed motion. The solid phase fraction does not affect the rate of bed subsidence.

7 Conclusions

The article begins with a brief sketch of development of carbonisation and wood gasification technology. Thermal treatment of biomass played a leading role in the development of iron smelting, artillery, and chemical industry,

which in the past were the most advanced branches of economy. Also the automotive revolution in the nineteenth century was connected with solid fuel processing, as the first engines were fuelled with syngas.

The article presents an overview of fundamental physical and chemical issues concerning reactors which gasify biomass in a sliding porous bed. Due to their highest productive potential, wood and straw were analysed in detail. Wood is characteristic for low ash content, while the amount of ash remained after straw gasification can reach 10%. Then, main structural types of gasifying reactors with porous bed are presented, and the gasification processes taking place in each of these reactors are analysed.

During the pyrolysis, wood and straw lose up to 80% of their solid substance, which turns into gas. Mass reduction observed in this process is accompanied by volume reduction, all this leading to the decrease of the apparent density of the solid substance. The temperature-dependent distribution of basic gas products of wood pyrolysis is presented. The diagram illustrates the increase of hydrogen production and the decreased contribution of carbon dioxide provoked by the temperature increase. It also shows that the carbon oxide curve has its maximum at the temperature of about 500 °C.

Also studied are basic mechanisms of combustion of pyrolytic gases, i.e., carbon oxide, hydrogen, and methane. A key role in the combustion reactions is played by free radicals, which control the rate and direction of the processes. Most important heterogeneous reactions of gases with the heated charcoal bed include: Boudouard reaction, carbon-steam reaction (water-gas reaction), and carbon-hydrogen reaction (methanisation).

The final part contains a three-dimensional description of motion of bed particles caused by changes of their volume. The analysis of motion of porous bed particles bases on the equation of the volume change of solid phase particles in Lagrangian coordinates, which has been transposed to Eulerian coordinates to obtain the equation in which the divergence of velocity of the bed particles is equal to the rate of changes of their volume.

Received 2 March, 2015

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