Catalytic pyrolysis of biomass of solid compounds used for gasoline production

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Abstract. The article examines the latest achievements of foreign researchers whose key focus is to obtain gasoline fractions from the biomass of solid compounds using catalytic pyrolysis for its further use in industrial sectors. The biomass of solid compounds is studied as a raw material for production of gasoline fractions due to its low cost and high availability. In addition, several ways for obtaining and converting biomass are studied. At high temperatures (up to 800° C) solid is used to produce synthesis gas by partial oxidation in an autothermal packed bed reactor over catalysts. Biomass is an acidic flammable liquid containing more than 300 compounds. Industrial biomass is not compatible with existing liquid transportation fuels, including gasoline and diesel. In order to use biomass as a conventional liquid transport fuel, it must be catalytically modernized.

1. Introduction
Due to its low cost and high availability, lignocellulosic biomass is being studied as a raw material for renewable liquid biofuels [1–4]. Lignocellulosic biomass is not used as a liquid fuel because economic processes of its conversion have not been developed yet [1]. Currently, several methods are being studied to convert solid biomass into liquid fuel. The production process includes several stages which significantly increases the cost of biomass conversion [5]. For example, the production of ethanol from lignocellulosic biomass involves several stages, including pretreatment, enzymatic or acid hydrolysis, fermentation, and distillation. The authors of the article [2] demonstrated that diesel range alkanes (DRA) can be obtained by treating the aqueous phase with aqueous solutions of carbohydrates at low temperatures (100–300°C) [6]. The solid lignocellulosic biomass is converted into aqueous carbohydrates which requires pretreatment and hydrolysis. At high temperatures (up to 800°C) [3], it was shown that solid biomass can be reformed to produce synthesis gas by partial oxidation in an autothermal packed bed reactor over Rh catalysts [7]. The ideal solid biomass conversion process involves production of liquid fuels from solid biomass in one step with a short residence time.

2. Materials and methods
The purpose of this work is to study the latest achievements of foreign scientists who study aromatic hydrocarbons from the gasoline range obtained from solid biomass raw materials in a single reactor for a
short residence period (less than 2 minutes) and at intermediate temperatures (400-600°C) using the method of rapid pyrolysis. Rapid pyrolysis involves rapid heating of biomass (up to 500°C) to intermediate temperatures (400-600°C), followed by rapid cooling (residence time in pairs is 1-2 s) [8]. Fast pyrolysis causes a thermally unstable liquid product - biomass which is an acidic combustible liquid containing more than 300 compounds [9].

Biomass is not compatible with existing liquid fuels, including gasoline and diesel. In order to use biomass as a conventional liquid transport fuel, it must be catalytically modernized [10–13]. The introduction of zeolite catalysts in the pyrolysis process can convert oxygen-containing compounds formed during the pyrolysis of biomass into gaseous aromatic hydrocarbons. Catalytic rapid pyrolysis involves the pyrolysis of solid biomass (for example, cellulose) into volatile organic compounds, gases, and solid coke. Then the organic matter is introduced into the zeolite catalyst, where they are converted into aromatic compounds: carbon monoxide, carbon dioxide, water and coke. Within the zeolite catalyst, biodegradable species undergo dehydration, decarbonylation, decarboxylation, isomerization, oligomerization and dehydrogenation which form aromatic substances, CO, CO₂ and H₂O.

The task of selective production of aromatics involves minimization of undesired coke formation which can be caused by homogeneous gas-phase thermal decomposition reactions or heterogeneous reactions on the catalyst. Stoichiometry used for conversion of xylitol and glucose into toluene, CO and H₂O is shown in equation (1) (carbon yield is 76 and 24%) and equation (2) (carbon yield is 63 and 36%), respectively. Oxygen must be removed from the biomass in combination of CO (or CO₂) and H₂O when aromatics are formed. The maximum theoretical yield of toluene from xylitol and glucose is 76 and 63%, respectively, when CO and H₂O are formed as by-products.

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\begin{align*}
C_5H_{12}O_5 & \rightarrow \frac{12}{22} C_7H_8 + \frac{26}{22} CO + \frac{84}{22} H_2O \\
C_6H_{12}O_6 & \rightarrow \frac{12}{22} C_7H_8 + \frac{48}{22} CO + \frac{84}{22} H_2O
\end{align*}
\]

Some of the previous researchers studied biomass conversion using zeolites [14–18], studied the conversion of aqueous solutions of carbohydrates over ZSM5 catalysts in a fixed bed reactor [14]. They obtained an aromatic yield of 18% (carbon) for aqueous glucose, and the remaining products of the reaction yield were CO, CO₂ and coke, taken separately, giving a total of less than aromatic (31%). ZSM5 is also added to the fluidized bed pyrolysis reactors [15]. The authors of [15] considered rapid pyrolysis of pine sawdust with ZSM5 in the reactor, and the yield of aromatic compounds of 12% (carbon) was observed. Other studies revealed that the organic liquid phase can be produced by pyrolysis of biomass with a zeolite-based catalyst, however, these studies did not quantify the composition of the organic phase [16–17]. Olefins and aromatics can also be obtained from thermally stable oxygenates derived from biomass (for example, glycerol) over catalysts based on zeolite [18], determined the effective ratio of hydrogen to carbon (H/C) as shown in equation (3) (H, C and O correspond to the number of atoms of hydrogen, carbon and oxygen, respectively). The H/C ratio of petroleum products obtained from 2 (for liquid alkanes) to 1 (for benzene).

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\frac{H}{C} = \frac{H - 20}{C}
\]

Experimental results (Biagini, Lippi, Tognotti) show that aromatics can be produced from solid types of biomass, 1) when choosing the proper catalyst, 2) using high heating rates and 3) using high catalyst ratios. The Pyroprobe reactor is described in (U.S. House of Representatives on H.R. 3030). Preliminary results (Biagini, Lippi, Tognotti) with Pyroprobe indicate that a nominal temperature of 600°C provides the highest yield of aromatics. Figure 1 shows carbon yield and aromatic selectivity for catalytic rapid pyrolysis of xylitol, glucose, cellobiose, and cellulose.

As can be seen, the main products include aromatics, CO, CO₂ and coke. No olefins were identified during catalytic rapid pyrolysis in the reactor system which differs from what was reported in sources [15, 17]. Xylitol gives a higher yield of aromatic compounds. Xylitol also has a higher H/C ratio (2/5) than other biomasses (for cellulose, glucose and cellobiose). The aromatic yield of these reactions is about half of the
theoretical yield determined by equations (2) and (3). Coke yield exceeds 30% for all these channels. Coke can be burned to provide process heat for the catalytic rapid pyrolysis reaction. 12% of the carbon raw materials obtained from solid biomass should be burned to provide process heat for catalytic rapid pyrolysis. Real biomass feedstock (wood, grass, etc.) requires more carbon to be incinerated, which depends on the water content and biomass composition. Aromatic distribution of resulting oxygenates are shown in Figure 1. The raw materials have similar distribution of the aromatic product when tested under the same reaction conditions. The motor octane number of the aromatics products is approximately 111 (based on the summation of individual aroma components). This aromatic product can be used as a fuel directly as a high octane fuel additive. In the US, aromatics are currently limited to 25% [20]. Aromatic substances can also be hydrogenated to cyclic alkanes in the secondary process. Hydrogen can come from steam reforming of coke deposits or from the reaction of carbon monoxide gas shift.

![Aromatic distribution of resulting oxygenates](image1)

**Figure 1.** Catalytic pyrolysis of cellulose, cellobiose, glucose and xylitol (reaction conditions: mass ratio to catalyst is 19, ZSM5 catalyst (SiO₂/Al₂O₃ = 30), the nominal heating rate is 1000 °C, the reaction temperature is 600 °C, the reaction time is 240 s).

The yield of aromatic compounds is halved, and the proportion of coke increases from 35 to 40% while the heating rate decreases from 1000 °C to 1 °C. High heating rates are likely to reduce undesirable thermal decomposition of the reaction. A time of 240 s at 600°C is required to achieve 100% conversion. At high heating rates, the biomass spends the maximum amount of energy at the above-mentioned reaction
temperature, thus maximizing the yield of liquid. Figure 2 shows product selectivity for catalytic rapid pyrolysis of glucose with ZSM5 depending on the mass of the catalyst and the ratio of glucose.

![Figure 2](image)

**Figure 2.** Carbon yield as a function of the nominal heating rate of catalytically fast pyrolysis of glucose with ZSM5 (reaction conditions: catalyst-to-feed weight coefficient is 19; catalyst ZSM5 (SiO₂/Al₂O₃=30), reaction temperature is 600 °C, reaction time is 240 sec): CO (■), aromatic hydrocarbons (▲), CO₂ (□), coke (•).

The yield of coke increases, and the aromatic yield decreases as the ratio of catalyst to glucose decreases. Thermally stable oxygenates are formed when the ratio of catalyst to glucose decreases. Oxygenates include furan, 2-methylfuran, furfural, 4-methylfurfural, furan-2-methanol, hydroxy-acetyl aldehyde, and acetic acid (Figure 2). The experimental unit does not identify thermally unstable compounds that are formed during the pyrolysis process. At high catalyst / glucose ratios, the main products hydroxyacetaldehyde and acetic acid; furan selectivity increases while the catalyst to glucose ratio decreases. These results indicate that in addition to aromatics, catalytic fast pyrolysis can be used to produce oxygenates which can be used as chemicals or fuel precursors. The right choice of catalyst is crucial for high aromatic selectivity.

Figure 3 shows the results of catalytic fast pyrolysis of glucose with various catalysts. The catalyst with the highest yield of aromatic compounds was ZSM5. In the absence of any catalyst, the main product is coke. The catalytic parameters that influence distribution of the product are the pore structure and the type of acid sites. We used ZSM5, silicalite and SiO₂-Al₂O₃ to test the relationship between catalytic parameters and catalytic activity. Silicalite and ZSM5 have the same pore structure, but different types of acidic sites. ZSM5 contains Brensted (Lewis Acid), but silicalite does not contain it. Silicon oxide contains Bronsted, but it is an amorphous material. Silicalite produces coke which indicates that Bronsted centers are required for production of aromatics. Silica is also produced mainly from coke which indicates that the pore structure of Zeolite is also required for selective production of aromatics.
3. Conclusion

The above-described experiments of foreign researchers were carried using a Pyroprobe reactor of the 2000 model analytical pyrolyzer (CDS Analytical Inc.). The probe is a computer controlled resistive heating element that holds an open quartz tube. Powder samples are stored in a tube with loose packing of quartz wool during pyrolysis, vapors flow out into the open ends of the quartz tube into a large cavity (interface pyrolysis) with a stream of helium carrier gas. The flow of particles from the carrier gas is directed to a gas chromatograph coupled with a mass selective detector. In the interface, pyrolysis was carried out at 100 °C. They used helium as inert pyrolysis gas. A constant flow program of 0.5 ml min⁻¹ was used for a GC capillary column (Restek Rtx-5sil MS). The Pyroprobe reactor was programmed to maintain the temperature at 50 °C for 1 minute. Products were quantified by introducing calibration standards into the system. The mole of carbon in the product is divided by the mole of carbon in the reagent. Carbon on the spent catalyst was determined quantitatively by elementary analysis and described in [20]. Missing carbon can be attributed to a thermally unstable compound that cannot be detected in the experimental setup under consideration. Powdered reagents were obtained by mixing carbohydrates and catalyst. Physical glucose mixtures were obtained using ZSM5 (SiO₂/Al₂O₃ = 30) to the ratio of d-glucose (Fisher) 19, 9, 4, 2.3 and 1.5. Xylitol (Fisher) cellobiose and cellulose were tested. ZSM5 was calcined at 500 °C in air for 5 hours.
before the reaction. Samples with a glucose catalyst equal to 19 were also obtained with the following catalysts: silicalite, b-zeolite, Y-zeolite (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}=25), mesoporous (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 4).

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