Obtaining a diesel fuel component from liquid products of oxidative pyrolysis of wood

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Abstract. Recycling and rational use of wood-processing industry waste is an urgent task for the economy and industry. On the basis of experimental studies on the oxidative pyrolysis of Siberian pine and Downy birch, a basic technological scheme for components of motor fuels obtaining is proposed. It is shown that the main components of liquid products of wood pyrolysis in water vapor are aromatic and saturated hydrocarbons, as well as oxygen-containing compounds that need to be hydrogenated.

1. Introduction
Russia is a major exporter of unprocessed timber. According to a report by Wood Resources International, timber exports in 2020 amounted to 15 million cubic meters. Preparing wood for transportation is always associated with sawing it, which leads to the formation of a large amount of sawdust. The Russian government is planning to introduce a total ban on the export of unprocessed timber from 2022. This means that exporting enterprises will be forced to produce various sawn timber, and this, in turn, will increase the volume of waste generated by the wood-processing industry, including sawdust. Sawdust can be used as a solid fuel, as a material for the manufacture of pressed products or in agriculture. Despite such widespread use of sawdust, in Russia there is a significant surplus.

An interesting, but still underdeveloped, way of recycling woodworking industry waste is to obtain carbon sorbents based on them. This is becoming more and more relevant with the tightening of environmental legislation in Russia and the world. An interesting method for the production of such sorbents is one-stage pyrolysis in a stream of water vapor, developed by the Bulgarian Academy of Sciences. The advantages of this method are obvious: carrying out pyrolysis and activation at the same time significantly reduces the energy consumption for the process [1,2].

When pyrolysis is carried out in a stream of water vapor, it interacts with the organic matter of the raw material, which leads to the formation of a large amount of liquid and gaseous products. The composition of liquid products largely depends on the characteristics of the feedstock, but contains a large amount of valuable organic substances [1,3-5], which can be used as valuable components of motor fuel [6]. Sawdust is a rather promising raw material for this process, since when adsorbents are obtained using the classical technology, they form a carbonizate with a well-developed surface, and also contain about 6% wt. hydrogen, which is practically quantitatively converted into liquid and gaseous products during pyrolysis.
The aim of this work is to study the liquid products of the pyrolysis process in a stream of water vapor of Siberian pine sawdust (Pinus sibirica) and Downy birch (Betula pubescens) as potential components of motor fuels.

2. Results and discussion

The composition of sawdust used as a raw material for pyrolysis in a stream of water vapor is indicated in Tables 1 and 2. Before analysis, the sawdust was dried at a temperature of 105 °C to constant weight.

Table 1. Elemental composition of sawdust.

| Timber species         | C, % wt | O, % wt | H, % wt | N, % wt |
|------------------------|---------|---------|---------|---------|
| Pinus sibirica         | 49.30   | 43.88   | 6.70    | 0.12    |
| Bétula pubescens       | 48.61   | 44.96   | 6.43    | -       |

Table 2. Results of technical analysis of sawdust.

| Timber species       | Ash, % wt | Moisture, % wt | Water extractable substances (90 °C), % wt |
|----------------------|-----------|----------------|------------------------------------------|
| Pinus sibirica       | 0.27      | 9.80           | 3.36                                     |
| Bétula pubescens     | 0.49      | 11.2           | 1.67                                     |

From the data presented, it can be seen that sawdust in its composition is different from each other. Especially in the content of nitrogen, which is found only in sawdust obtained from Siberian pine, as well as in the number of substances extracted by hot water. The content of such substances is higher in the case of Siberian pine as well.

The study of the yield and composition of liquid products of the thermal oxidative process destruction of sawdust of various tree species was carried out on samples with a particle size of more than 2.5 mm. Pyrolysis in a stream of water vapor was carried out in one stage on the installation shown in Figure 1.

Figure 1. Diagram of a coal pyrolysis plant in a steam flow: 1 - steam boiler; 2 - reactor; 3 - furnace; 4 - thermocouples; 5 - cooler; 6 - receiver; 7 - water jacket

The plant consists of a reactor placed in the furnace, a unit for preparing and regulating the supply of water vapor, a unit for separating pyrolysis products and devices for temperature control and analysis of pyrolysis gases. This installation allows you to regulate the amount of supplied water
vapor, as well as the conditions of the experiment. The optimal conditions were selected on the basis of the data presented in [7, 8] (atmospheric pressure, temperature - 700 °C, heating rate - 10 °C/min).

The liquid products obtained in the process were separated from the condensed water. Further, their structural and group composition was determined. The analysis consisted in the separation of substances that make up the liquid products of oxidative pyrolysis according to the classes of organic compounds (carboxylic acids, phenols, organic bases, neutral compounds, etc.). The resulting neutral substances were analyzed using an HP 6890 gas chromatograph equipped with an MD 5973 mass detector. The analysis was performed on an HP1MS capillary column, 35 meters long, with 0.25 µm film thickness. Experimental conditions: sample injection temperature - 85 °C, final temperature - 320 °C, temperature rise rate - 5 °C/min, detector temperature - 300 °C. Helium was used as a carrier gas; the gas flow rate was 1.2 ml/min. The boiling range of the neutral fraction was also determined.

The yield of products from oxidative destruction of sawdust is presented in Table 3. The material balance of the process is calculated without taking into account water condensed during pyrolysis in a stream of water vapor.

| Timber species         | Carbon residue % wt | Liquid Products, % wt | Gas, % wt |
|------------------------|---------------------|-----------------------|-----------|
| Pinus sibirica         | 23.62               | 60.18                 | 16.2      |
| Betula pubescens       | 17.9                | 58.3                  | 24.1      |

Sawdust from Siberian pine forms a greater amount of liquid products and the carbon residue, characterized by a well-developed surface (918 m²/g) compared to the wood of Downy birch. This suggests that this wood is a more valuable raw material for this process.

The results of the structural group analysis of liquid products are shown in Table 4.

| Timber species         | Neutral oil | Acids | Phenols | Organic bases | Losses |
|------------------------|-------------|-------|---------|---------------|--------|
| Pinus sibirica         | 41.80       | 37.75 | 17.70   | 1.55          | 1.20   |
| Betula pubescens       | 46.93       | 33.00 | 19.15   | 0.02          | 0.9    |

Table 4 shows that the structural-group composition of liquid pyrolysis products in a stream of water vapor differs significantly from the composition of liquid products of traditional wood pyrolysis. First of all, attention is drawn to the high yield of neutral substances. This suggests that oxidative pyrolysis at a temperature of 700 °C leads to a significant transformation of the organic matter of wood. It can be assumed that the resulting polar organic substances are destroyed under the action of high temperature with the formation of gaseous products. As evidence, we can cite the composition of the gaseous products of oxidative pyrolysis of Siberian pine wood (Table 5).

The results of gas chromatography-mass spectrometry are shown in Figure 2. The analysis results are recalculated taking into account the yield of neutral oil and are indicated in mass percent.

| Timber species | CO₂ | CmHn | CO | H₂ | CH₄ |
|----------------|-----|------|----|----|-----|
| Pinus sibirica | 64.1| 23.5 | 12.1 | 0.1 | 0.3 |
Liquid products formed during pyrolysis in a stream of water vapor of Siberian pine wood, in comparison with the same products from Downy birch sawdust, contain more paraffins and furan derivatives. Fluid birch products are enriched with naphthalene, as well as ketones, alcohols and naphthenes, components and naphthenes. Determination of boiling points showed that neutral oils boil away in the boiling range of diesel fuel. The beginning of boiling of neutral oils was 204, 232 °C for neutral products obtained from downy birch and Siberian pine, respectively. The end of the boiling point of these fractions are around 360 °C. The studies carried out show that neutral components of liquid products from wood pyrolysis in a stream of water vapor can be used as components of diesel fuel. However, such products contain a large number of oxygen-containing products (up to 12 % wt), which will require additional purification. This can be done in a standard hydrotreating process that is widely used in domestic refineries. In this case, saturation of aromatic compounds will also occur, which will favorably affect the quality of the resulting fuel component.

A schematic flow diagram of the processing of liquid products from oxidative pyrolysis into a diesel fuel component is shown in Figure 3.

In accordance with the proposed schematic diagram of the technological process, the first three operations are associated with the removal of various polar organic substances from liquid pyrolysis products. To do this, they are sequentially washed with the-13% NaHCO3 solution, the 10% NaOH solution and the sulfuric acid solution with a concentration of 10% wt. As a result of washing, sodium salts of carboxylic acids, sodium phenolates and salts of pyridine bases are formed, respectively. These products are highly soluble in water and are removed together with the wash water. The resulting neutral components are washed with clean water and fed to rectification to remove moisture and light low-boiling components. After that, a necessary stage of processing is the hydrotreating of the obtained products from oxygen-containing compounds and aromatic components, since their presence negatively affects the operational properties of diesel fuels. Traditional nickel-molybdenum or cobalt-molybdenum sulfide catalysts can be used in this process, since both performed well in the purification of middle hydrocarbon distillates. The product stream after hydrotreating is directed to stabilization to remove dissolved hydrocarbon gases and rectification, where a diesel fuel component is obtained.
Figure 3. Basic technological scheme for obtaining a diesel fuel component from liquid products
of oxidative pyrolysis of wood.

3. Conclusion
The data presented in the article show that liquid products of pyrolysis of wood from different
varieties in a stream of water vapor can be used to obtain a component of diesel fuel. The main
operations in its production are extraction with aqueous solutions of acids and alkalis, hydrotreating of
neutral organic substances and rectification.

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