

Determination of the fraction composition of bio-oil products in a laboratory device

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Abstract: The article analyzes the separation of Bioneft by different methods, and the differences between the physical and chemical properties of petroleum substances. At the beginning of 1960, the capacity of the pyrolysis plant for ethylene was 100-140 thousand tons per year, and by the present time, this indicator is more than 1.0-1.4 million tons per year. The final drying of light diesel fuels is carried out with small-particle sodium sulfuric acid or calcium-chlorine granules and filtered. The temperature of the pyrogas in the reactor at the exit from the reactor is found by the following equation. They are presented as catalytic, initiated, thermal contact, and hydrolysis methods.

1 Introduction

The technology of more effective use of biomass in bioenergy is direct burning, incineration; pyrolysis; gasification; produce of methane by anaerobic fermentation; alcohol and motor fuel, and oil production. Technologies of biomass use, providing energy in a convenient form for the consumer, are constantly being perfected to the maximum possible level of efficiency [1].

In general, energy is obtained from organic waste either by physical, chemical, or microbiological methods: by physical method, energy is obtained by burning organic waste; the basis of the chemical method is the use of the process of prolysis and gasification; biogas production by pyrolysis. An extremely valuable product of biogas production is obtaining high-quality active coal. In the technological process, biomass is heated at a high temperature without oxygen in a special reactor-methane tank, so that full (maximum) methane release is ensured [2].

2 Materials and methods

Pyrolysis is a high-temperature cracking, which is mainly used to obtain ethylene and other unsaturated hydrocarbons, depending on the type of raw materials used (natural gas, gas condensate, kerosene, gas oil, naphtha) at a wide range of temperatures (600–1200 °C), practically at 670–720 °C and atmospheric As a result of deep decomposition of fractions with kerosene or kerosene at high pressure and secondary processes, up to 50% gas (containing 30% alkanes) and 45-47% oil remain, compared to the properties of ~74~ raw

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materials. After refining the oil, 20% benzene, 16% toluene, and 2% xellol are obtained, and they are used as individual substances after further purification [3].

Pyrolysis is one of the most essential methods of obtaining raw materials in the industry for petrochemical synthesis. Fractionation refers to the separation of complex mixtures into components that have a simple composition or a separate (individual) structure. Such separation of bio-oil by different methods embodies the difference between the physical and chemical properties of petroleum substances [1-15].

For these purposes, in most cases, the difference in boiling point (driving, rectification); the rate of evaporation, which mainly depends on the molecular mass (molecular driving and thin layer evaporation); tendency to adsorption in various porous bodies (chromatography); solubility of various solvents (extraction); (crystallization from solutions) melting temperature, etc. Sometimes separate methods are generalized in fractionation; for example, extraction and extraction (extractive extraction (razgonka), or, adsorption and rectification (hypersecretion), adsorption and extraction (analysis of waxy substances), and hoses [5].

The primary method of fractionation of motor fuels and hydrocarbon gases in the technical analysis of oils is separation by boiling point, that is, driving and rectification.

Determining the fractional composition of petroleum products in standard devices. The boiling point and especially the boiling point characterize the starting property of 10% fuel. The lower this temperature, the more volatile substances in the fuel and the easier it is to start the engine in the cold at slightly lower temperatures. Based on Razgonka data, the starting of engines at the lowest temperatures has an empirical formula [6].

During the period of development of thermal pyrolysis of hydrocarbons, a number of important improvements were made to the design of pyrolysis furnaces and the technological scheme of production. In this regard, at the beginning of 1960, the capacity of the pyrolysis plant for ethylene was 100-140 thousand tons/year, and by the present time, this indicator is more than 1.0-1.4 million tons/year.

Bionefit products contain water in some cases, they must be cooled and separated before use. The final drying of light diesel fuels is carried out with small-particle sodium sulfuric acid or calcium-chlorine granules and filtered. To dry heavy types of fuel, it is heated up to 500 °C and filtered several times in a granular layer of table salt consisting of large crystals [7-15].

During the pyrolysis process, the temperature increases over time. After 70 minutes, it was noted on the graph that the temperature did not exceed 500 °C (figure 1).

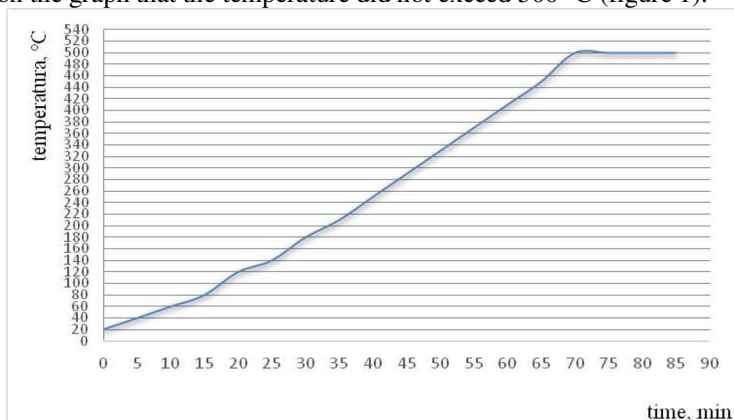


Figure 1. Time dependence graph of the temperature of the pyrolysis process.

3 Results and discussions

Calculation of the heat balance of the zmeevik tube reaction pyrolysis device of the gradient type. A fraction with propane was obtained for the pyrolysis device, and its composition is shown in the table 1. The composition of pyrogas from raw materials is also shown in the table below. Production capacity of the pyrolysis device $G=5$ kg/hour. Propane fraction pyrolysis is carried out with an additional $Z=2$ kg/hour of steam. The temperature of the raw material at the entrance to the oven is $T=298$ K [8].

Table 1. Propane fraction for pyrolysis device.

Components	Content; mole %		Components	Content; mole %	
	Propane fraction feedstock	Pyrolysis		Propane fraction feedstock	Pyrolysis
H ₂	0.7	13.2	C ₃	10.7	8.9
CH ₄	6.3	33.6	C ₃	56.7	4.1
C ₂ H ₂	-	0.3	C ₄	4.1	0.9
C ₂ H ₄	4.9	27.3	C ₅	-	2.1
C ₂ H ₆	16.6	9.6			

Composition of raw materials and pyrogas. The molecular mass $M_r = 39.2$ density $\rho_r = 1.75$ kg/m³ of raw materials is molar mass of pyrogas $M_p = 23.8$ density $\rho_p = 1.07$ kg/m³.

We calculate the molecular mass of the mixture of raw materials and water vapor at the entrance and exit of the zmeevik:

$$M_k = \frac{12000}{366.9} = 32,7; \quad M_r = \frac{12000}{530.68} = 22.6 \quad (1)$$

The temperature of the pyrogas in the reactor at the exit from the reactor is found by the following equation.

$$T = T_2 X_2 + T_3 X_3 + T_3 X_3 + T_4 X_4 \quad (2)$$

Here: T_2, T_3, T_4 - temperatures of hydrocarbons ($C_2 H_6, C_3 H_6, C_3 H_8, C_4 H_{10}$) at the outlet of the reactor, K; X_2, X_3, X_4 - amount of carbohydrates in ($C_2 H_6, C_3 H_6, C_3 H_8, C_4 H_{10}$) raw material.

The final temperature is directly related to the contact time, which is reflected in the Schmidt formula:

This is for ethane,

$$Lg \tau = -12.75 + \frac{13700}{T} \quad (3)$$

This is for propane, propylene and butane,

$$\lg \tau = -10.96 + \frac{11038}{T} \quad (4)$$

Where is τ ; τ the optimal contact time (hours).

The total time is related to the optimal time as follows.

$$\tau_{total} \leq (1.8 \div 2.1) - \tau_{exp} \quad (5)$$

Here, using the table, we take $\tau_{total} = 0.7$ hours.

$$\tau_{exp} = \frac{\tau_{total}}{2.1} = \frac{0.7}{2.1} = 0.33 \text{ } ^\circ C \quad (6)$$

$$\lg 0.33 = -12.75 + \frac{13700}{T_2} : \Rightarrow T_2 = 1117K; T_3 = 1055K \quad (7)$$

$$\lg 0.33 = -10.96 + \frac{11038}{T_3} \quad (8)$$

We calculate pyrogas temperature T by looking at the amount of hydrocarbons ($C_2 H_6, C_3 H_6, C_3 H_8, C_4 H_{10}$) in the raw material from the table.

$$T = 1117 \cdot 0.1363 + 1055 \cdot 0.1230 + 1055 \cdot 0.6755 + 1055 \cdot 0.0652 = 1063K \quad (9)$$

The development of raw material processing processes does not stop and constantly requires functional improvement aimed at reducing economic and operational costs, as well as increasing the profitability of target products. To achieve these goals, scientists are conducting research on improving existing processes. Along with the introduction of modifications, several fundamentally new methods of pyrolysis have been proposed. They are presented in the form of catalytic, initiated, thermal contact, and hydrolysis methods [10].

Differential heat and gravimetric analysis. Thermogravimetric and differential thermal analyzes (Tg and DTA) of the considered types of raw materials are analyzed during pyrolytic processing in an inert environment. It is brought to air-dry condition beforehand for analysis. The heating rate is 10°C per minute. It is used to determine the yield of semi-

coked products during slow pyrolysis corresponding to the average heating rate. The slow type of pyrolysis was chosen mainly because of the formation of a carbonaceous residue and the formation of char accompanied by heat-releasing reactions. [8]

In the experiment, a temperature range of 20 to 600°C was obtained. The final temperature is determined after the completion of all exothermic reactions of the raw material. The amount of heat needed for pyrolysis was calculated according to the above method, according to which the amount of heat given to dry raw materials (Q_1), the temperature of raw materials before the beginning of decomposition (t_1). The amount of heat is given to the raw material (Q_2), for the formation of carbon residue (Q_3) and volatile pyrolysis products - gas, pyrogenetic water vapor and tar (Q_4).

The heat of exothermic reactions occurring during the heating of raw materials is sufficient to heat to cover the above costs. Autothermality is the amount of heat needed to heat the exothermic reactions occurring in raw materials. Temperature ranges of exothermic reactions are determined by t_{exo}^S t_{exo}^f , °C. From the peaks in the DTA curve, the value of the heat effect on the dry mass of the raw material was obtained. The value of the total heat effect ($\sum Q$) reflects the difference between the heat output from exothermic reactions and the heat losses (Q_{1-4}). Specific heat is determined in the analyzer. The heat capacity of the carbon residue is assumed to be equal. 0.105 kJ/(kgK) for cottonwood and 1.5 kJ/(kgK) for wood waste.

Determining of thermal properties of the studied raw materials the results were presented. It should be noted that wood waste has a high value for biomass, and cottonwood has high ash has low ash due to its quantity. All types under consideration high yield of volatile substances in raw materials shows the stability of the organic part of the material at low temperature and low temperature, which is confirmed by the information in the literature.

Volatile substances begin to emerge from the stalk at a temperature of 100°C, and a dried stalk can spontaneously combust even at a temperature of 115°C.

Based on the obtained curves, the values of the quantities needed to calculate the heat costs were determined. Tg+DTA was conducted to study the heat effects occurring in raw materials during pyrolysis. The temperature of complete evaporation of moisture corresponds to the end of the endothermic peak on the DTA curve, and the moisture content (W^a) is considered equal to the weight loss at this temperature. At the temperature of the beginning of decomposition of the raw material (t_1), the increase in the rate of weight loss corresponds to the beginning. Calculation of heat costs was carried out for several temperatures from the interval t_1-t_p .

The value of the mass of carbon residue formed at temperature t_1 was calculated by subtracting the moisture content from the total mass of raw materials, including the release of volatile substances.

The mass of carbon residue for the final temperature of pyrolysis of raw materials was determined from the Tg curve, and the yield of volatile products is the difference between the values of the mass of carbon residue at temperatures t_1 and t_p .

Table 2. Initial data for heat calculation.

Fuel	Characteristic						
	t_d , °C	W^a , %	t_1 , °C	C_{pb} kDJ/kg	t_{exo}^S	t_{exo}^f , °C	Q_{HE}/Q_{TE}
Organic waste of small horned animals	110	8	230	2.37	240-550		1062
Wood shavings	110	6	230	2.29	240-570		1103
Guza stem	105	6	180	1.5	200-570		393
Pine tree leaves	105	7	180	1.6	200-530		862

The results of calculating heat costs are presented in the table. It should be noted that for wood waste, the heat value required to heat the raw material (Q_2) to the temperature of the beginning of active decomposition is twice as high as that of wood. This is due to the large heat capacity of wood, which is related to the chemical composition of the raw material. Wood shavings contain more organic substances (table 2), which have a higher specific heat capacity than mineral substances. In addition, Q_2 is quite different with heat-treated and wood waste. Wood shavings make up a third, compared to sapwood, which contains less than 10%. This is done by calculating the results of the material balance of different types of biomass. It can be seen that the maximum yield of tar, which is a product of the thermal decomposition of raw materials, is greater than that of wood shavings. Because it is the most thermally stable component that strengthens the walls of plant cells, the active decomposition of wood raw materials requires heating to high temperatures. In this regard, the same value of t_1 in the processing of wood waste is higher than 50°C in the processing of hemp. Organic waste of small horned animals and wood shavings begin to decompose actively after heating to 230°C and 400°C , they lose the main part of the raw material mass during the pyrolysis process. This is because in this temperature range all the main components of wood, cellulose, and hemicellulose, decompose together [5].

Volatile gases, on the other hand, begin immediately with a rise in temperature, after which there is a uniform loss. The heat for the formation of valuable carbon residue (Q_3) in wood processing is also higher, compared to wood pulp, the heat capacity of carbon residue is high. Losses with variable products (Q_4) rise to a temperature of 300°C , and during the pyrolysis process, when the temperature is increased, more volatiles are formed and then light gases are released [4].

4 Conclusions

The development of raw material processing processes does not stop and constantly requires functional improvement aimed at reducing economic and operational costs, as well as increasing the profitability of target products. To achieve these goals, scientists are conducting research on improving existing processes. Along with the introduction of modifications, several fundamentally new methods of pyrolysis have been proposed. They are presented as catalytic, initiated, thermal contact, and hydrolysis methods.

In conclusion, every country has 3 underground resources - gas, oil, and coal reserves, and 4- pyrolysis fuel as fuel contributes to the enrichment of underground reserves.

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