Utilization and biodegradation of wastes

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Receiving liquid and gaseous fuel from brown coal and waste tires

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Abstract – The possibility for obtaining liquid and gaseous fuels by the method of combined pyrolysis of energetically unfavorable brown coal and waste tires is considered and a catalytic system for them is developed. The pyrolysis was carried out at atmospheric pressure, using local natural zeolites instead of expensive metal catalysts. Pyrolysis experiments were carried out in a fixed-bed-reactor at various temperatures (300 to 600°C).

Keywords: brown coal, polymer waste, pyrolysis, zeolite catalysts, catalytic cracking, petroleum products, aromatic compounds.

Утилизация и биодеградация отходов

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Получение жидкого и газообразного топлива из бурого угля и отработанных шин

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Рассмотрена возможность получения жидкого и газообразного топлива методом комбинированного пиролиза энергетически неблагоприятных бурых углей и углеводородных отходов на разработанной авторами каталитической системе. Пиролиз проводили при атмосферном давлении с использованием местных природных цеолитов вместо дорогостоящих металлических катализаторов. Эксперименты по пиролизу проводили в реакторе с неподвижным слоем при различных температурах (от 300 до 600°C).

Ключевые слова: бурый уголь, отходы полимеров, пиролиз, цеолитные катализаторы, каталитический крекинг, нефтепродукты, ароматические соединения.

INTRODUCTION

The search for methods of processing coal, integrated with the use for the needs of the energy, economic, and chemical potential of the country, is due to the increasingly complex energy and environmental problems of using coal in the national economy, as well as the development of innovative technologies. Such techniques have been used and will be used hereinafter to be useful for producing high quality products in the resolution of the above problems.

The search for effective technologies based on the use of local raw material resources is particularly pressing problem in anticipation of reducing the world's primary source of fuel resources – oil, and countries like the Republic of Armenia does not possess oil fields and coal deposits have.

The nonbiodegradable nature of polymer material makes its disposal difficult. Waste tires cause a variety of environmental and health challenges as they are bulk and non-degradable. The major methods used in waste tire management differ according to economic costs and industrial usage [1–6]. We have previously shown that catalytic pyrolysis of plastic and the tires in the presence of zeolite catalysts increased the formation of the aromatic components. Among the studied natural catalysts, clinoptilolite from the Noyemberyan deposit RA was most active [4–6]. Potential solutions to address the waste tire problem are pyrolysis, gasification and liquefaction processes.

The purpose of this study is to obtain fuel with a higher heat value. We have tried to achieve this by carrying out pyrolysis of brown coal in the presence of natural zeolites of Armenia (more specifically, clinoptilolite), as well as using oil waste obtained during the pyrolysis of automobile tires and some polymer residues.

MATERIALS AND METHODS

Brown coal is a soft, brown, combustible, sedimentary rock formed from naturally compressed peat. It is considered the lowest ranking coal because of its relatively low heat capacity. It is mined all over the world and is used almost exclusively as a fuel for steam power generation. According to the results of geological exploration works carried out in the territory of the Republic of Armenia (in generaly in the north part of country), at present there are several dozen deposits of brown coal.

Brown coal is brownish-black in color and has a carbon content of 20 – 25 to 60 – 70 percent, high moisture sometimes up to 75 percent and ash content of 6 – 19 percent compared to 6 – 12 percent for bituminous coal [7, 8]. The heat value results of some fuel are given in table 1 [9].

The process was carried out in the laboratory conditions according to the following scheme. The principle of equipment operation is as follows: crushed waste, catalyst and, if necessary, the solvent mixture is given in retort (2), where under conditions of atmospheric pressure the conversion occurs under the influence of heat.

Table 1. The heat value results of some fuel [9]

Fuel type	The heat value (Specific heat of combustion) MJ / kg
Peat	8.1 – 9.0
Fire wood (dry)	11.0 – 16.0
Brown coal	10.0 – 17.0
Hard black coal	23.9 – 24.0
Petrol/gasoline	44.0 – 46.0
Diesel	42.0 – 46.0

The evaporated vapors are raised through the plates placed in gas-liquid separator (4) and condensing and flowing into the reception area to the condenser (3). Uncondensed gases are accumulated in the gasgolder (5) and are returned to the reactor providing the heat of the reactor (Fig. 1).

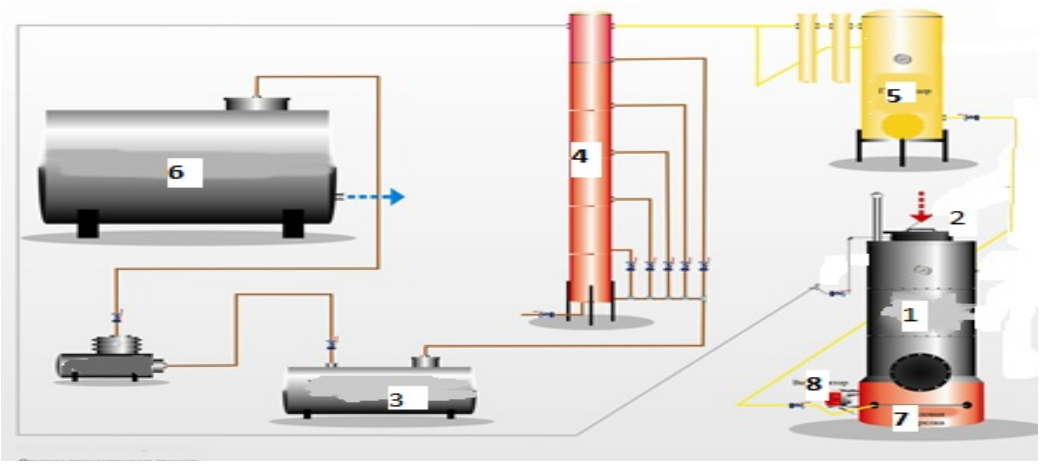

Fig. 1. The equipment used in the technological scheme. 1 – Oven; 2 – Retort; 3 – Condenser; 4 – Gas-liquid separator; 5 – Gasgolder; 6 – Fluid collection; 7 – Gas burner; 8 – Injection system.

The following installation is proposed for pyrolysis of brown coal (Fig. 1), the preliminary tests of which showed that from 1 kg of coal at T = 400 – 450°C, P = 1 atм, 0.35 – 0.40 l/kg of liquid condensate is obtained.

At the same time, depending on the raw material composition, after the reaction is over, the surplus of the combustion gas can be used as a gas fuel in other sectors where it is needed.

RESULTS AND DISCUSSION

Pyrolys process of worn tires

Previously, the catalytic liquefaction process of tires has been studied on this equipment, with 40% yield of oil with varying content [2, 3].

Liquid-chromatographic analysis and fraction dissociation have been previously studied by the composition of the obtaied liquid product. The obtained liquid fuel is essentially a mixture of aromatic and heterocyclic compounds containing about 70% (mass) aromatic carbohydrates, up to 10% (mass) of saturated and unsaturated carbohydrates and solid residues of about 20% (mass). The preliminary assessment of the pyrolysis results is summarized in Table 2.

Table 2. Preliminary assessment of pyrolysis results of worn tires, characteristics of products [2, 3]

Fraction	Quantitative yield, % from dry raw materials	The average heat of burning
Liquid	30 – 70	28 MJ/kg
Gas	20 – 60	30 MJ / m^3
Solid Carbon remainder	10 – 20	40 MJ/kg

Pyrolysis of rubber material involves the thermal degradation at high temperatures (250…900°C) in an oxygen-absent environment. It can be performed under vacuum or atmospheric pressure. The scheme of the experiment is shown in the figure above. In table 3 shows the amount of liquid products depending on temperature. As a result of catalytic processing of worn tires, hydrocarbon gases and liquid products were obtained.

Liquid product (38…55% wt. of feedstock) also known as pyrolyzed tire oil or biocrude is the most significant product of the process. It is obtained from the condensation of vapor of a pyrolysis reaction and can be used as diesel fuel oil or as raw materials for organic and petrochemical synthesis, including the production of automotive fuel. To this end, the liquid products were subjected to distillation at atmospheric pressure. As a result, fractions were obtained which boiled out at temperatures of 180…320ºC and a bottom residue, which is a dark, low-viscosity liquid (table 4).

The bottoms were then returned to the cycle and used as a source of hydrogen, for the pyrolysis processes of brown coal. A solid pyrolysis residue in the form of a powder can be used as an additive to the asphalt mixture in road construction. To determine the optimum conditions for the catalytic liquefaction process, the effect of the reaction temperature and the ratio of the initial reactants to the yield of the desired liquid product was studied. Analysis of the results shows that the content of the catalyst in the range of 10…20% wt. affects the yield of liquid products, and also increases the yield of aromatic compounds (table 3).

Table 3. The composition of the samples and the yield of liquid products of worn tires pyrolysis

Temperature, °C	Content of initial components, % wt.			The yield of liquid products from the organic mass of the mixture, %
	Worn tires	Pasteurizer (Bottom residue from tires pyrolysis)	Zeolite	
300	50	50	0	38.2
300	45	45	10	52.2
300	40	40	20	52.5
350	45	45	10	48.8
350	40	40	20	50.5
350	30	60	10	55.1
400	30	60	10	49.8

Structurally grouped liquid pyrolysis products are presented in Figure 2. Such pyrolytic oil can be used directly as a fuel and as an important source of chemicals in the chemical industry due to the high concentration of benzene, toluene.

Experimental data on the catalytic pyrolysis of rubber in the presence of zeolite catalysts were obtained using the same process as the analogous reforming process, which, in turn, leads to the formation of aromatic components.

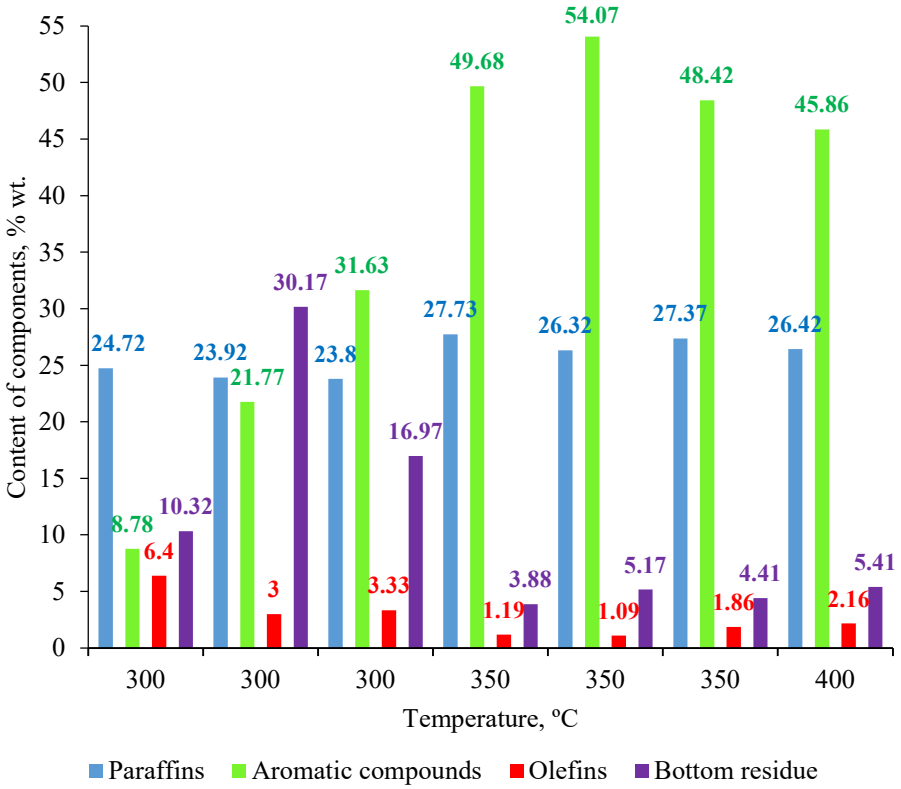

Fig. 2. Structurally grouped of liquid products *(*from table 3, the yield of liquid products from the organic mass of the mixture, %) of pyrolysis of worn tires

Pyrolysis process of brown coal and copyrolysis of brown coal with a residue of worn tires

For the pyrolysis of brown coal and copyrolysis of brown coal with a residue of worn tires proposed flow-sheet technology, there are obtained 0.30 – 0.40 l/kg liquid condensate from 1 kg of lignite (main component of brown coal) at 400 – 450°C.

The composition of the liquid condensate (from 0.30 – 0.40 l/kg liquid condensate from 1 kg of brown coal) in accordance with the gas-liquid analysis are presented in table 4.

Table 4. The liquid products obtained after brown coal's catalytic pyrolysis. The yields and composition

№	Liquid organic materials	Yield, %
1.	Paraffins $C_{11} – C_{25}$	20.0 – 23.0
2.	Olefins	1.5 – 4.5
3.	Phenol and its derivatives	22.0 – 24.0
4.	Benzene and its derivatives	5.5 – 7.0
5.	Bicyclic compounds	30.0 – 34.0
6.	Polycyclic compounds	14.0 – 18.0

Table 5 shows the results of copyrolysis of brown coal with a residue of worn tires. The maximal output of liquid products goes to 300…400°C, and the increase in temperature is negligible, but does reduce the output of the product. It relates to the process of decomposition, as the outputs of gaseous products and lightweight fractions increase.

Table 5. Results of copyrolysis of brown coal with a residue of worn tires

Temperature, °C	Content of components, *% wt.*			
	Gas	Liquid	Solid	Losses
300	2.67	74.78	20.40	2.15
400	3.92	75.77	18.33	1.98
500	4.82	68.87	21.35	4.96
600	6.42	65.96	24.03	3.59

The heat value of the liquid was estimated in region 30 – 31 MJ/kg, which accounted for 70% of diesel fuel.

The cost of the obtained fuel is about 260 AD (0,5$)/l. It is cheaper than diesel fuel, but with its heat providing it yields to it. This fuel can be used as stove fuel in greenhouses.

This liquid hydrocarbon mixture can also be used as raw material in organic compounds, carbohydrates, household chemistry, and others. This kind of research is also needed for the produced gas.

CONCLUSION

This study provides valuable findings under selected experimental conditions for energy recovery, indicating that brown coal and worn tires can be used as alternative energy sources. It is possible to achieve economic gain with the elimination of an environmental problem during the using of solid waste after pyrolysis as best additional agent for pyrolysis of brown coal as basic initial component for obtaining alternative fuel.

КОНФЛИКТ ИНТЕРЕСОВ
Авторы заявляют об отсутствии конфликта интересов.

CONFLICT OF INTERESTS:
The authors declare no conflict of interests.

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