Int. J. Chem. Sci.: 14(1), 2016, 261-268
ISSN 0972-768X
www.sadgurupublications.com

OBTAINING OF LIQUID FUEL FROM COAL IN THE PRESENCE OF THE POLYMERS

D. A. BAISEITOV, SH. E. GABDRASHOVA, A. K. AKYLBAI, O. DALELKHANULY, ZH. B. KUDYAROVA, L. R. SASSYKOVA, M. I. TULEPOV[*] and Z. A. MANSUROV

Al-Farabi National University, ALMATY, KAZAKHSTAN

ABSTRACT

Coal hydrogenation was carried out at an elevated pressure of hydrogen in the presence of polymers forming pastes (tar, polyethylene and crumb rubber). It is found that when the content of the polymeric material in the mixture less than 10.0% by wt. conversion rate of the mixture in the liquid and gaseous products is not high, which prevents the effective implementation of the process. The degree of coal conversion and the yield of light boiling products are increased with increasing of amount of synthetic resin material in a mixture up to 70.0% per mix weight. The highest indicators of conversion degree of coal (72.1 wt.%) and the yield of liquid products (50.4 wt.%) were observed for composition the mechanical activated coal/tar/concentrate of Balkhash field: 45/45/10. The developed method in the work of producing of liquid from coal products allows to increase an yield of the light boiling hydrocarbon fraction from 12.0 up to 60.0% by mass.

Key words: Coal, Polymers, Hydrogenation, Forming a paste, Catalysts.

INTRODUCTION

The most perspective way of synthesis of liquid products from coal is a direct hydrogenation, or effect on coal with the molecular hydrogen under pressure at the increased temperature with use of liquid products (paste-formers) and catalysts[1,2]. In the course of hydrogenation there is a destruction of coal substances and their saturation (hydrogenation) with change of the fractional and chemical composition.

When the hydrogenation nearly 90% of the coal is converted into gas and liquid products, high-boiling (boiling point above 300-350°C) are recycled in the process and the final product is a distillate having a boiling point of 300-350°C (a mixture of raw gasoline,

---

[*] Author for correspondence; E-mail: tulepov@rambler.ru

kerosene, diesel fuel) and containing 60-65% of the organic mass of carbon[3-5]. It is known that for transformation of organic mass of coal into liquid products, it is necessary to carry out destruction of coal macromolecules and to increase concentration of hydrogen in them, it is usually reached by heating of coal under pressure of molecular hydrogen in the medium of forming of a paste possessing hydrogen-donating properties. Such polymers as polyethylene and polypropylene, contain about 14.0 wt.% of hydrogen. In the course of joint thermo transformation with coal they can serve as a potential source of hydrogen required for the conversion of coal into the light boiling hydrocarbon fractions. Furthermore, thermal cracking of polyethylene and polypropylene proceeds by a radical mechanism. In the course of their joint thermal transformation with coal there is an interaction of radical fragments of thermal destruction of coal with the radicals of polymer that prevents the secondary reactions of polymerization and polycondensation of the coal products leading to formation of coke[4,5].

The aim of this work was to study the hydrogenation of coal in the presence of a paste-forming polymers and investigation of their effect on the process.

EXPERIMENTAL

Experiments on coal hydrogenation were carried out in a rotating 0.5-liter autoclave with the method developed in the laboratory[6]. The mixture of coal, polymer and catalyst was downloaded into the autoclave, was sealed and flushed with argon for air removal. Thereafter, hydrogen was pumped into the autoclave to 5.0 MPa and heated to 430°C. Duration of the process was 1 hr. After exit of the autoclave on the regime, in these conditions the pressure in the autoclave was equal to 8.0-10.5 MPa. As a paste-forming were investigated tar, polyethylene and rubber crumb. After completion of the experiment the autoclave was cooled and the volume of the gaseous products was determined. Consumption of hydrogen gas was calculated from the difference in its quantity in the autoclave before and after the experiment. The condensed part of the products was taken from the autoclave and separated on malthenes, extracted with hexane, asphaltenes, extracted with benzene, and the solid residue. By quantity of the solid residue and its ash-content counted the extent of transformation of the organic mass of coal (OMC) into gaseous and liquid products. For the qualitative and quantitative analysis was applied the method of gas chromatography: GLC KNAUER - for the liquid fraction and "Chromatec - Crystal 5000" for gas. X-ray fluorescent researches and the element analysis of a solid sample were carried out on the microanalyzer FOCUS-M2M with use of Fe-radiation in the range from 2.0 to 37.0 V. Intensity of diffraction maxima was estimated by an analytical method in a tetragonal singoniya. Changes of a surface and structure were defined by the scanning electronic microscope of Ntegra Therma with the lighting modes - "on a gleam" and "on reflection".

RESULTS AND DISCUSSION

In the present work studies were carried out to determine the effect of the amount of polymers, the forming of paste, on the obtaining of liquid products from coal. For research, mixture of coal, forming of paste and iron-containing concentrate of Balkhash field (Kazakhstan) was prepared. Concentrate contained in its composition Fe - 32.80%, S - 15.53%, and was subjected to mechanochemical treatment. The resulting mixture was heated under hydrogen pressure from 1.0 to 5.0 MPa with subsequent isolation of the desired products.

It is found that the hydrogenation of coal in tar, which has a hydrogen-donor properties the investigated catalysts greatly increase the degree of OMC conversion (Table 1). The highest indicators of conversion degree of coal (72.1 wt.%) and the yield of liquid products (50.4 wt.%) were observed for composition the mechanical activated coal/ tar/concentrate: 45/45/10.

Table 1: Hydrogenation of coal in the present of forming of paste

Composition (coal, tar, concentrate of Balkhash field), wt.%	Degree of conversion of OMC (wt.%)	Yield of gaseous products (wt.%)	Yield of solid products (wt.%)	Hydrogen consumption (vol.%)
Coal/tar: 50/50	68.1	42.1	5.8	0.5
Coal/tar/concentrate: 45/45/10	65.1	43.5	5.7	1.5
Mechanical activated coal/tar/concentrate: 45/45/10	72.1	50.4	5.4	1.8
Mechanical activated coal/polyethylene/ concentrate: 80/10/10	70.2	44.2	6.8	1.9
Mechanical activated coal/rubber crumb/ concentrate: 80/10/10	69.2	45.2	6.1	2.0

When using the catalyst applied in the high-disperse form on a surface of brown coal in the presence of polyethylene and a rubber crumb rather low indicators of transformation of coal were received. Evidently, this is due to the fact that activated iron is present in the form of difficult complexes at structure of polymers of polyethylene and a rubber crumb, and it can create certain diffusive restrictions for products of thermal destruction of coal. In the conditions of process of a hydrogenation tar is dehydrogenated, turning into liquid hydrocarbons. Possibly, dehydrogenation of tar in the presence of coal results from its interaction with OMC or products of its thermal destruction.

Data of oscillatory spectroscopy of initial coal showed (Fig. 1) that these compounds belong to amorphous formations. In particular, the organic component of coals represents mixture of various X-ray amorphous components, presence and quantity of which changes among the raw of metamorphism. Physico-chemical characteristics of the resulting polymer with coal, in particular, the Raman spectrum showed that the major product is mainly composed of carbon (not less than 90%) and to 10% of the mineral impurity entering a basis of polymeric material (Fig. 2).

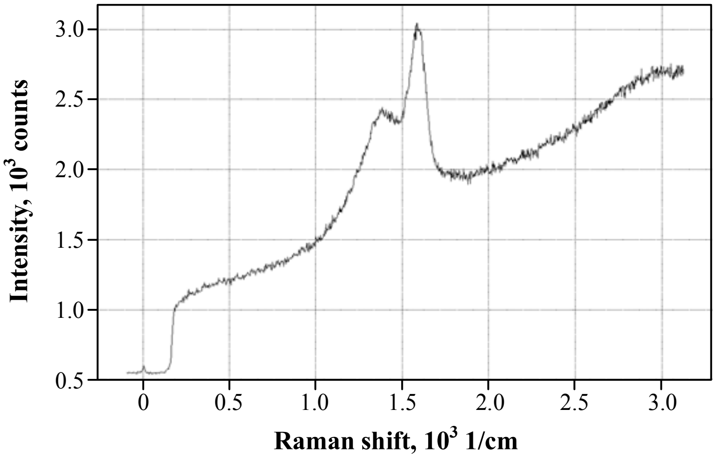

Fig. 1: Raman spectrum of initial carbon materials

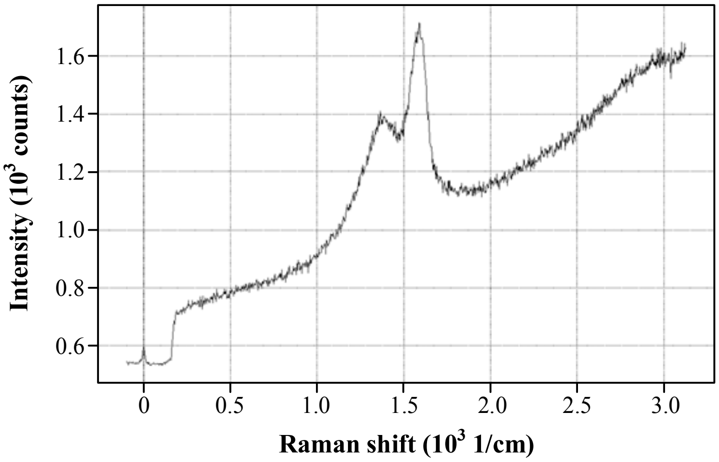

Fig. 2: Raman spectrum of coal with a polymer (polyethylene)

According to gas chromatography the gaseous products of hydrogenation of coal represented mainly carbon oxides, the content of hydrocarbon gas of C_1-C_4 does not exceed 20.0 vol. % (Table 2). In the course of a hydrogenation there is a consumption of molecular hydrogen with coal. It can be concluded that a sufficiently high yield of hydrocarbon gases takes place in the presence of polymers, i.e., in cases where the free hydrogen possess in abundance. Allocation of CO_2 after a hydrogenation is explained by processes of decarboxylation of polymers, emergence of hydrocarbonic gases promotes to the deep destructive processes of organic synthesis of a liquid phase and substance of coal with immediate filling of uncompensated bonds with the allocated hydrogen.

Table 2: Chromatographic analysis of hydrogenation products

Compound	Initial	In the presence of polymer
The liquid phase (vol.%)		
C_2H_5OH	3.3	2.6
C_6H_6	8.4	9.4
$C_6H_5CH_3$	10.4	10.9
p-xylene	7.0	6.4
Ethyltoluene	8.1	6.0
Ethylbenzene	4.6	6.6
Gaseous phase (vol.%)		
H_2	18.1	24.3
CO	3.6	5.1
CO_2	13.2	19.1
CH_4	7.5	6.7
C_2H_6	2.1	1.8
C_2H_4	-	1.0
C_3H_8	1.2	0.9
C_4H_{10}	1.3	1.0

Thus, presence of polymer at coals leads to allocation of the flying and soluble low-molecular products, which are products of destructive transformations of coal and polymers. The quantitative yield, composition and a structure of products of reaction depend on the condition of a hydrogenation, a stage of carbonification of coal, medium, a type and the mode of mechanical influence.

At the hydrogenation of tar and coal the increase in quantity of liquid products and depth of transformation of organic mass of coal is observed.

Table 3: Influence of polyethylene and composition of the mixture on yield of liquid products of hydrogenation

Composition	Quantity of polimer in the mix (wt.%)	Degree of conversion (wt.%)	Yield of the products of liquid fractio (wt.%)	
			$T_{boiling}$<200°C	$T_{boiling}$ >200°C
Mechanical activated coal/ polyethylene/concentrate: 80/10/10	10.0	70.2	5.2	44.2
Mechanical activated coal/ polyethylene/concentrate: 70/20/10	20.0	71.6	10.3	45.4
Mechanical activated coal/ polyethylene/concentrate: 50/40/10	40.0	75.2	23.7	37.5
Mechanical activated coal/ polyethylene/concentrate: 30/60/10	60.0	77.0	32.5	40.5
Mechanical activated coal/ polyethylene/concentrate: 15/75/10	75.0	78.0	30.7	48.0
Mechanical activated coal/ tar/concentrate/polyethylene : 10/10/10/70	70.0	73.1	52.4	10.2
Mechanical activated coal/ tar/concentrate/polyethylene : 10/5/10/75	75.0	72.1	60	8.3

Increase of extent of conversion of coal and of the yield of liquid products from coal, improvement of composition of the obtained liquid products, decrease of working pressure of process of hydrogenation of coal is feasible in the presence of catalysts or catalytic additives, which accelerate transfer of hydrogen from donor solvent to the organic mass of coal and activate molecular hydrogen, transferring it into atomic form.

It is found that at addition of concentrates of Balkhash field consumption of coal by hydrogen from tar was 1.5-2.0% from OMC on material balance, according to the chromatographic analysis of gaseous hydrogen - 1.3-1.5% of OMC. In the environment of polyethylene the forming of paste having the ability to dissolve the coal hydrogenation products, but not having hydrogen and donating properties, the degree of OMC conversion significantly less than that obtained in the medium of tar.

Results of research showed that dehydrogenation of polyethylene in the studied conditions doesn't happen. Thus, the difference in the indicators of non-catalytic conversion of coal of tar in the medium and polyethylene characterizes the contribution of hydrogen-donor properties of the forming of paste to the overall process. In the environment of a rubber crumb unlike polyethylene addition of the studied catalysts to coal leads to reduction of extent of conversion of OMC, but increase of the yield of liquid products. It is probable that in this case the catalytic effect is caused by hydrogenation of products of destruction of coal with molecular hydrogen on a catalyst surface[7,8].

The yield of liquid products with a boiling temperature below than 200°C is equal to 12.0 wt.% per the weight of the loaded mixture (Table 3). The yield of liquid product with boiling points above 200°C - is 30 wt.%. The degree of conversion of the mixture into liquid and gaseous products, as determined by the weight of the solid residue was 70.0.

At increase in amount of polyethylene in mix to 75.0% the yield of liquid products of joint transformation of coal with polyethylene with a temperature of boiling below 200°C maximal was 37.0% by weight, and products with a temperature of boiling above 200°C was 48.0% by weight, conversion of mix into liquid and gaseous products thus was 78.0% by weight.

CONCLUSION

Thus, the coal hydrogenation at an elevated pressure of hydrogen in the presence of polymers, forming pastes (tar, polyethylene and a rubber crumb). Presence of polymer in coals leads to allocation of the flying and soluble low-molecular products which are products of destructive transformations of coal and polymers. It is found that at the content of polymeric material in mix less than 10 masses. % extent of conversion of mix in liquid and gaseous products is low that interferes with effective implementation of process. The degree of coal conversion and the yield of light products increases with increasing of amount of synthetic polymeric material in a mixture of up to 70.0 % per mix weight. Further increase of the content of polymeric material in the mixture does not significantly change these parameters of the process. In the present work, the developed method of obtaining of liquid products from coal allows to increase the yield of the low-boiling hydrocarbon fraction from 12.0 to 60.0 wt.%. An advantage of the present process of producing of liquid products from coal is the high yield of hydrocarbon products boiling up to 200°C, the exception from the technological scheme of the process stage of isolating and hydro refining of the forming of paste, and the possibility of recycling of industrial and domestic wastes of the polymer materials.

REFERENCES

1. A. A. Krishko, Hydrogenation of Coal of USSR, M, CSRIEI Coal, 110 (1984) (in Russ.).
2. A. S. Maloletnev, Production of Synthetic Liquid Fuel Through Hydrogenation of Coals, M., Nedra, 128 (1992) (in Russ.).
3. E. C. Atherton, Polyamide Supports for Polypeptide Synthesis, J. Am. Chem. Soc., **97**, 65-84 (1975).
4. J. W. Hellgeth and L. T. Taylor, Coal Liquefaction of Bituminous Coal, Fuel, **63**, 961-967 (1984).
5. E. J. Kuhlmann and D. Y. Jung, Coal Liquefaction using a Hydrogenated Creosote Oil Solvent, H-Atom Transfer from Hydrogen Donor Components in the Solvent, Fuel, **64**, 1552-1557 (1986).
6. M. Tulepov, Hydrogenations of Coal of the Kiyaktinsky Field after Mechanoactivation, Eurasian Symposium on Innovation in Catalysis and Electrochemistry, Almaty, Abstracts, 86 (2010) (in Russ.).
7. M. Tulepov, Physico-Chemical Characteristics and Reaction Ability of the Dispersed Coals, News of the Academy of Sciences of RK, Series of Chem. Technol., **5**, 76-82 (2010) (in Russ.).
8. V. V. Boldyrev, K. Tkacheva and Ju. T. Pavljukhin, Research Structural Change in Mechanically Activated Chalcopyrite with NGRS, Reports of the USSR Academy of Sciences, Chemical series, **273**, 643-649 (1983) (in Russ.).

Accepted : 15.12.2015