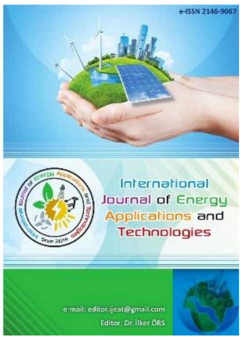
International Journal of Energy Applications and Technologies 8(3) [2021] 93-97

e-ISSN: 2548-060X

International Journal of Energy Applications and Technologies

journal homepage: www.dergipark.gov.tr/ijeat



Original Research Article

Investigation of the improvement of Sivas-Kangal lignites liquefaction product yields

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ARTICLE INFO

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Received May 12, 2021
Accepted September 7, 2021

Published by Editorial Board Members of IJEAT

doi: 10.31593/ijeat.936840

ABSTRACT

In recent years, converting and using coal into the most suitable product according to its properties has emerged as a modern approach. Among the main processes applied to coal are low and high-temperature carbonization, gasification and liquefaction. In coal liquefaction, coal is broken down into free radicals using hydrogen donor solvent and catalyst under high temperature and pressure conditions. Later, these radicals can be used in the production of both liquid fuel and chemical raw materials by being saturated with hydrogen. This study aims to improve the yields of Sivas-Kangal lignite liquefaction products (char, preasphaltene, asphaltene, oil-gas). For this purpose, firstly raw coal, then spiral enriched clean coal liquefaction experiments were carried out. The chemical characterizations of the obtained products were determined by proximate and ultimate analysis. The composition of the oil was identified by GC-MS. As a result of the enrichment, the char yield decreased by 16.5% whereas the oil+gas yield increased by 14.64%. Total conversion increased from 31.74% to 48.24%. It has been concluded that the enrichment process has a positive effect on the liquefaction yields.

Keywords: Asphaltane; Lignite; Liquefaction; Oil; Preasphaltane

1. Introduction

Because of the organic and inorganic compounds contained in coal, it is important not only to meet the energy need but also to be a source of chemical raw materials. For this reason, various processes such as pyrolysis and liquefaction have been tried to produce solid and liquid fuels or chemical raw materials from coal. There are many studies on this subject in the literature [1-6].

The structure of coal is different from that of the hydrocarbons in petroleum. The principal difference between coal and petroleum is due to the lower H/C ratio of coal. The H/C ratio is not just the molar H/C ratio, but the molar ratio of H/C after subtracting the H needed to eliminate N, S and O from the product [7]. Therefore, to convert coal into liquid products it is necessary to increase the H/C ratio in the products compared with the original coal. This is accomplished by direct hydrogenation or by the removal of carbon. Indirect liquefaction processes involve the gasification of coal in a fixed or fluidized bed reactor followed by the conversion of the synthesis gas into liquid hydrocarbons. Catalytic liquefaction processes are carried out in the presence of active catalysts to produce hydrocarbons directly, and the rehydrogenation of solvents occurs in situ. When catalysts are not used, the process is usually known as solvent extraction. Solvent extraction has been used for many years as a useful method to investigate coal structure. In catalytic and non-catalytic processes, coal is slurried in a coal-derived solvent and heated to 400-500°C for varying lengths of time. Since, in non-catalytic processes, coal minerals may also play the role of catalyst, and both processes are essentially hydroliquefaction processes, the distinction between the two processes is actually not justified [8].

The material extracted from coal may be separated into various fractions according to its solubility in a particular solvent (such as hexane, toluene, THF). It was decided to use the classification of oils (soluble in hexane), asphaltenes (soluble in toluene) and preasphaltenes (insoluble in toluene) for this study [9, 10].

In the present study, Kangal lignite liquefaction studies were carried out in non-catalytic conditions in a nitrogen gas atmosphere. The effect of the enrichment process of the liquefaction products was investigated by comparing the product yields.

The material extracted by coal/solvent contacting was Soxhlet extracted successively by tetrahydrofuran (THF, C_4H_8O), hexane (C_6H_{14}), and toluene (C_7H_8) to yield oil, asphaltene, and preasphaltene respectively.

In the literature, there are some investigations related to the liquefaction product yields of the lignite [11-13]. However, the effect of the enrichment in the liquefaction process on the properties of the obtained products has not been fully studied yet.

2. Materials and Methods

The lignite sample used in this research was acquired from Kangal-Sivas, which is located in the Internal Anatolia of Turkey. The lignite samples were prepared according to the ASTM standards (ASTM D3173, ASTM D3174 and ASTM D3175) for gross calorific value, proximate and elemental analysis.

The spiral tests were performed using a Reichert spiral with 5-launders. The tests were done at different size fractions (-3.35+2, -2+1.18 and -1.18+0.15 mm), different solid/liquid ratio (7.5, 15, 25 and 35% solid by wt.) and different splitter settings (90, 120 and 150°). The cleanest coal obtained as a result of these experiments was used for liquefaction. The results of the proximate and elemental analysis of raw and clean coal of Kangal lignite are given in Table 1.

Table 1. Proximate and elemental analysis results of raw and clean coal of Kangal lignite (on air-dried basis)

Component	Raw coal	Clean coal
Moisture (%)	5.83	4.98
Ash (%)	43.66	20.41
Volatile matter (%)	31.91	12.34
Fixed C (by difference) (%)	18.60	62.27
Total S (%)	2.94	1.29
Elemental analysis		
C (%)	22.81	35.41
H (%)	1.40	2.84
N (%)	0.36	0.45
S (%)	2.95	1,97
O (by difference) (%)	72.48	59.33
H/C molar ratio	0.74	0.96
Higher heating value (kcal/kg)	2860	3990

The samples were ground and the -106 micron size fraction was employed for liquefaction. Tetrahydrofuran (Merck, 99.0%), tetralin (Merck, 98%), n-hexane (Riedel-de Haen, 95%), toluene (Riedel-de Haen, 99.7%), ethylene glycol (EG), acetone, and ethanol were used in the study. Liquefaction experiments were done using a mechanically stirred and electrically heated closed system 500 cm^3 stainless-steel Parr reactor (PARR-USA Brand Model 4575). For each experiment, 30 g of the coal was put into the Parr autoclave and 90 cm^3 of tetralin ($C_{10}H_{12}$) without any catalyst was added on it, and the autoclave was sealed and the pressure was adjusted to 20 bar by N_2. The autoclave was heated at about 3-4 °C/min and waited for 2 hours at 400 °C. It was mixed at a constant speed of 400 rpm during both heating and reaction. The autoclave was heated until 400°C at 60 min and then cooled to room temperature into an ice-water bath. The char, asphaltene, preasphaltene, and oil were separated from each other using the Soxhlet solvent extraction and evaporator system. The flow chart for the classification of coal liquefaction products is given in Figure 1. Total conversions of liquefaction products were calculated according to the results of solvent extraction and char yields. The effect of the enrichment on the properties of the liquefaction products and oil yield was determined using mass balance equations.

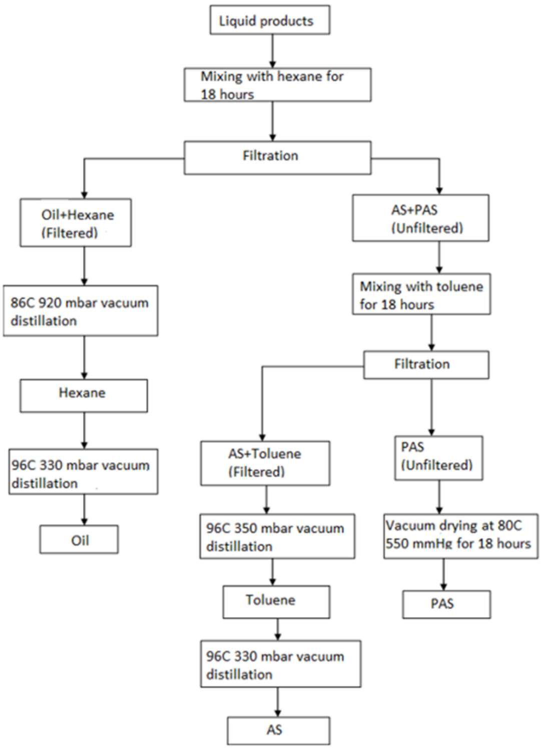

Fig. 1. Flow chart of coal liquefaction

Characterization and chemical structure of the liquefaction products were subjected using CHNS Elemental analyzer device (Leco CHNS 932, LECO Corporation, St. Joseph, MI), IKA C-1 calorimeter, Agilent Technologies 6890 N Network GC System model gas chromatography, and Agilent Technologies 5973 inert Mass Selective Detector mass spectrometer (Agilent Technologies, Santa Clara, CA) at the laboratory of Inonu University Scientific and Technology Center Research.

3. Result and Discussion

The proximate analysis results of the char of raw and clean coal are given in Table 2.

The elemental analysis results of the liquefaction products (char, preasphaltane and oil) of raw and clean coal are given in Table 3. Elemental analysis and calorific values of asphaltene products cannot be determined due to the difficulty of removing them from glass systems and the amount of material is small.

Table 3 shows that the C content and calorific value of all products in clean coal are increased. Therefore, it can be said that the enrichment process has a positive effect on liquefaction products.

Table 2. The proximate analysis results of the char of raw and clean coal

Char	Raw coal	Clean coal
Ash (%)	25.08	20.41
Volatile matter (%)	18.03	15.06
Fixed C* (%)	10.68	29.37

*by difference

In Table 4, the yield and total conversions of the products obtained as a result of liquefaction of raw and clean coal are given.

According to Table 4, while asphaltane and oil+gas yields increased in clean coal, the preasphaltane yield was unchanged. The total conversion of clean coal has increased. GC-MS chromatogram of oils is given in Figure 2 and Figure 3, and chemical compounds in Table 5.

As seen in Table 5, the main compounds of the oil were determined as saturated n-alkenes, isoprenoids, branched alkenes, n-alkyl cyclohexane, terpene and other aromatic structures, like the literature data [10, 14-17]. Also, the enrichment process was found to not affect the oil composition.

Table 3. Elemental analysis results of the liquefaction products of raw and clean coal

	Raw coal char	Clean coal char	Raw coal preasphaltane	Clean coal preasphaltane	Raw coal oil	Clean coal oil
Elemental analysis (%)						
C	51.10	64.72	72.16	79.21	73.46	85.14
H	3.65	5.36	5.59	6.56	7.02	8.96
N	1.70	1.18	1.19	1.34	0.41	0.30
S	2.54	1.82	0.92	0.71	0.39	0.26
O*	41.01	26.92	20.14	12.18	18.72	5.34
H/C	0.86	0.99	0.93	0.99	1.15	1.26
Higher heating value (kcal/kg)						
	6903	7083	7817	7961	4374	4991

*by difference

Table 4. The yield and total conversions of the products obtained as a result of liquefaction of raw and clean coal

Yield (%)	Char	Preasphaltane	Asphaltane	Oil+Gas	Total conversion
Raw coal	68.26	10.62	3.33	17.79	31.74
Clean coal	51.76	10.80	5.00	32.44	48.24

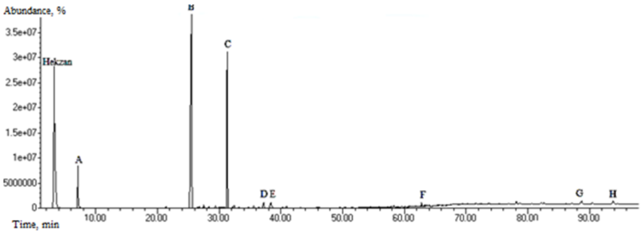

Fig. 2. GC-MS chromatogram of the obtained oil as a result of liquefaction of raw coal

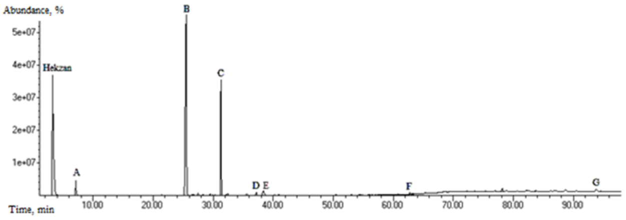

Fig. 3. GC-MS chromatogram of the obtained oil as a result of liquefaction of clean coal

Table 5. GC-MS analysis of the oil obtained from liquefaction of raw and clean coal and the detected compounds in the oil structure

Peak No	Retention time (min)		Probable Compound		Abundance (%)	
	Raw coal	Clean coal	Raw coal	Clean coal	Raw coal	Clean coal
A	7.101	7.129	Toluene	Toluene	6.38	2.50
B	25.485	25.497	Naphthalene, 1,2,3,4-tetrahydro, Tetraline	Naphthalene, 1,2,3,4- tetrahydro, Tetraline	53.54	59.55
C	31.293	31.287	Azulene Naphthalene	Azulene Naphthalene	30.42	25.61
D	32.634	32.631	Naphthalene, 1,2,3,4-tetrahydro-1-propyl	Naphthalene, 1,2,3,4-tetrahydro-1-propyl	0.84	0.86
E	37.215	37.232	Naphthalene, 2-methyl Naphthalene, 1-methyl	Naphthalene, 2-methyl Naphthalene, 1-methyl	1.28	0.73
F	62.775	62.781	Benzen,1,3-diethyl-5-methyl	Benzen,1,3-diethyl-5-methyl	0.68	0.40
G	88.673	93.783	2,2’-binaphthalene, 1,1’, 2,2’, 3,3’, 4,4’- octahydro-	1,2,3,10,11,12-hekzahydro perlin 7,8,9,10,11,12-hekzahydro benzo [a]piren	1.37	1.03
H	93.794		7,8,9,10,11,12-hekza hydro benzo [a]piren		1.28	

4. Conclusion

In the liquefaction studies with raw coal, char yield was 68.26%, preasfaltene yield was 10.62%, asphaltene yield was 3.33% and oil + gas yield was 17.79%. As a result of the liquefaction of the clean coal, the char yield decreased by 16.5%, the asphaltene yield increased by 1.67% and the oil + gas yield increased by 14.64%, while the preasphaltene yield remained unchanged. Total conversion increased from 31.74% to 48.24% (Table 3).

The calorific value of all products in clean coal is increased (for char from 6903 kcal/kg to 7083 kcal/kg, for preasphaltene from 7817 kcal/kg to 7961 kcal/kg, for oil from 4374 kcal/kg to 4991 kcal/kg).

According to GC-MS results, the main compounds of the oil were determined as naphthalene and its derivatives, tetraline, azulene, binaphthalene and benzene. In the oil of clean coal, no compounds were found that did not exist in raw coal. As seen in Table 4, the clean coal oil yield for the liquefaction process was founded as 32.44% to be higher than the raw coal oil yield (17.79%). From these results, it has been found that the enrichment process has a very positive effect on the liquefaction products, especially on the oil + gas yield.

Finally, it was suggested that the production of a more valuable product using the lignite having low calorific value will not only contribute more to the country's economy but also be better for the environment. However, it is necessary to investigate the economics of the theoretically and practically possible liquefaction method.

Acknowledgment

I would like to express my gratitude to my supervisor Assoc. Prof. İsmail Bentli for all his guidance and helpful advice throughout this study. The research presented in this publication was funded by the Inonu University Scientific Research Projects (BAP) unit (Project No. 2015/34).

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