Research Article GU J Sci, Part A, 10(2): 166-175 (2023) 10.54287/gujsa.1256330

Gazi University
Journal of Science
PART A: ENGINEERING AND INNOVATION
http://dergipark.org.tr/gujsa

Asphaltite Pyrolysis in Fluidized Bed Reactor

Samad MOGHANIRAHIMI[1*] Hüseyin TOPAL[1]

[1]*Gazi University, Faculty of Engineering, Ankara, Türkiye*

Keywords

Asphaltite
Pyrolysis
Fluid Bed
Liquid Fuel

Abstract

In this study, the pyrolysis properties of asphaltite samples taken from Şırnak and Hakkari regions in a fluidized bed reactor under catalyst and non-catalyst conditions were determined by rapid and batch pyrolysis. Basic analysis, FTIR and XRF analyses were performed for the raw material. GC-MS analysis methods were used for liquid pyrolysis products and FTIR were used for solids. In order to acquire the condition of the highest liquid product yield in pyrolysis, several effective variables such as particle diameter, vacuum, nitrogen flow rate, temperature, raw material feed rate, catalyst type, raw material type and duration were experimented and the results were evaluated. In general, the vacuum effect has led to an increase in liquid product yield and a decrease in gas product yield. Liquid product yield increased at 700°C pyrolysis temperature in continuous feed system and 550 - 650°C in batch system. In the pyrolysis studies carried out, a maximum liquid product yield of 16.5% was achieved in the continuous fed reactor at 700°C temperature, 400 mmHg vacuum, 2 g/min feed rate and 500 µm particle size.

Cite

Moghanirahimi, S., & Topal, H. (2023). Asphaltite Pyrolysis in Fluidized Bed Reactor. *GU J Sci, Part A*, *10*(2), 166-175. doi:10.54287/gujsa.1256330

Author ID (ORCID Number)

0000-0002-3737-1345 Samad MOGHANIRAHIMI
0000-0001-7406-4398 Hüseyin TOPAL

Article Process

Submission Date	25.02.2023
Revision Date	03.04.2023
Accepted Date	04.04.2023
Published Date	15.06.2023

1. INTRODUCTION

Gao et al. (2022) investigated bed agglomeration in pyrolysis of biofat-derived fuels in fluid bed. Biocoal, methanol, biooil, methanol fuels, whose yield was found to be lower than bio-oil, were used as inputs. The agglomeration yield due to the resulting tar yield and formation showed a positive linear correlation. Li et al. (2023) investigated the contribution of the joint delivery of oxygen and nitrogen to the system in two frit fluid bed reactors in pine sawdust oxidative rapid pyrolysis, the effect on the yield, formation and distribution of bio-oil, as well as its light and heavy components. Bilgin (2021) the effects of reagents by flotation enrichment process of asphaltite coal were examined. In the results of the experiments, it was determined by adding 100 g / t fuel oil reagent to reduce the sulfur rate. The sulfur content was reduced from 6.46% to 5.71%.

Kosan et al. (2021) have studied ammonia adsorption on asphaltite ash and thermodynamic approach on issues such as physical and chemical adsorption capacities, decrease in ΔH and ΔS, decrease in endothermic chemical adsorption, progression of increased exothermic physical adsorption reaction. Hameed et al. (2023) developed and simulated a CFD (Computational Fluid Dynamics) model to study cellulose pyrolysis using two different kinetic schemes in a fluidized bed reactor and to combine reaction kinetics with hydrodynamics. It was determined that the frequency factor and activation energies affected the yield of pyrolysis product. The yield of coal and tar increased, the fraction of gases decreased at high activation energy. Sezer et al. (2008) in the experiments in flash pyrolysis system, the content of the liquid product was thinned and classified by GC-MS analysis and the highest yield of the liquid product was tried to be reached under different test conditions. The solid residue was also analyzed as FT-IR, showing that the constant percentage of carbon and ash increases

*Corresponding Author, e-mail: s.mughanli@gmail.com

with temperature. In the pyrolysis study conducted by Sert et al. (2011) raw and demineralized Şırnak asphaltite was examined in terms of liquid product yield and determination of the amount of volatile matter at different temperatures. Hamamci et al. (1997) Turkey has reserves of approximately 77.5 million tons of asphaltite. In their experimental studies, Şırnak and Hazro tried to remove the sulfur of asphalt with the "Meyer Method".

Taskesen, et al. (2022) An investigation was conducted to obtain natural humic acid from the content of asphaltite samples taken from the reserve of asphaltites commonly found in Şırnak-Uludere Region. Demirci et al. (2019) Comprehensive information such as the formation of asphaltite resources in 13 regions of Turkey, the fact that it is known as an important resource due to valuable elements such as molybdenum, nickel and vanadium in it, its use in a 405 MW fluid bed thermal power plant, its inconvenient domestic use, its high caloric value, and the elimination of environmental risks due to its sulfur content are given.

One of the original aspects of this research is the study of thermal and catalytic pyrolysis of asphaltite in a fluidized bed reactor. One of the main objectives of the study is to obtain maximum liquid products and to contribute to growth of the country's economy in the future because of their hydrocarbon content. Another aim is to ensure that the by-products (gas, solids, etc.) obtained in the pyrolysis process can be recovered in the future by using environment friendly technologies. In addition, the main purpose of the liquid pyrolysis products to be obtained is to produce liquid products that do not create environmental pollution and will be possible to burn with high efficiency in classical combustion systems. In this way, a significant contribution will be made to the use of domestic resources, which are important for the country, in the energy field. Therefore, it is important for the environment and economy that asphaltites, which have large reserves in our country and have rich hydrocarbon content, are brought back to the Turkish industry by using combined technological methods such as pyrolysis, catalytic hydrocracking, hydrodealkylation, etc. in the future.

2. MATERIAL AND METHOD

In this study, the pyrolysis properties of asphaltite in a fluidized bed reactor under laboratory conditions were examined thermally and by use of catalysts in continuous feed and batch systems, accompanied by fluidizing nitrogen gas. By using three different asphaltite samples as raw materials in the pyrolysis process, various temperature, vacuum pressure, particle size, nitrogen flow rate, feed rate and catalyst effect were experimentally investigated. The average temperature distribution of the reactor was determined by thermocouple in nitrogen environment, nitrogen-free, vacuum and non-vacuum conditions and the suitability status was clarified before the experiments. The laboratory experimental system diagram is shown in Figure 1.

The rapid pyrolysis test system consists of DC motor, reductor, hopper and auger, tubular stainless steel reactor with a length of 30 cm and a diameter of 3.8 cm, a 1200 watt heater furnace, condenser, separator, digital gas meter, vacuum pump and automatic control system. In the discrete system, the DC motor, reducer, hopper and auger are removed from the system. In order to examine the physical-chemical properties and to be used in experimental studies, asphaltite samples were reduced to four different particle sizes (100, 200,... micrometer) with the help of sample crushing, grinding machine and sieve. The raw material supply speed was realized with the help of DC motor and reducer. Nitrogen gas is supplied to the system from under the reactor with a perforated metal plate distributor in order to prevent the stuttering of the asphaltite and to fluidize it. The minimum fluidization rate of nitrogen was calculated from Ergün's equation as 0.01001 m/s and the flow rate as 0.75 Lt/min.

3. EXPERIMENTAL STUDIES: CONCLUSIONS AND INTERPRETATIONS

Raw material and product analyzes, test conditions and analysis results and interpretation were made.

3.1. Investigation of Asphaltite Samples

Samples were simplified, FTIR and XRF (X-ray fluorescence), samples were obtained from those regions through Hakkari and Şırnak Universities.

3.1.1. Brief Analysis

The results of moisture, ash, volatile matter and constant carbon analysis of asphaltite samples are presented in Table 1. The sulfur content in the samples was determined in the XRF analysis.

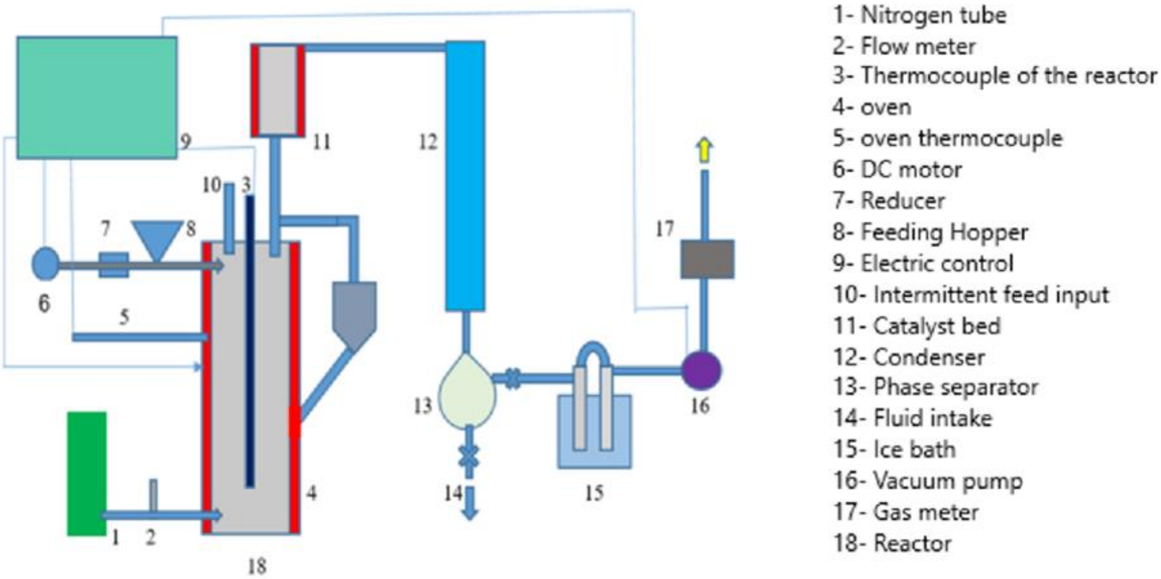

Figure 1. *Laboratory pyrolysis test system*

Table 1. *Brief Analysis of Samples*

	Humidity %	**Ash %**	**Volatile matter %**	**Fixed carbon %**
Hakkari-1 sample	2,60	35,28	45,42	16,7
Hakkari-2 sample	1,59	35,42	35,70	30,29
Şırnak sample	3,11	31	34,04	31,85

3.1.2. FTIR Analysis

The molecular structures of the Hakkari-1, 2 and Şırnak samples were examined by the FTIR method, and since the results were similar, only the IR spectrum of the Hakkari-1 sample was presented in Figure 2. As can be seen from the results, the IR spectra of all three asphaltite samples are close to each other, based on either to their peak levels or their frequencies. In addition, the most effective peak frequency in all three spectra is approximately in the range of 3000-2900 cm^{-1}. The frequency of the less effective peak next to it is 2900-2800 cm^{-1}. Both peak frequencies are generally thought to belong to carbon and hydrogen bonds (C-H), i.e. alkanes (Paraffins). Less effective peaks in the IR spectra of raw material quantities 1, 2 and 3 and frequencies from 1600-1400 cm^{-1} are considered to levels belong to C = C bonds, that is, mainly to aromatic hydrocarbons.Thus, although there are certain differences in the efficiency of the peaks in the IR spectra of the samples, the frequency ranges of all three asphaltites are very close. Therefore it is possible to accpet that all three asphaltite samples are mainly composed of various alkanes and aromatic hydrocarbons.

3.1.3. XRF Analysis

XRF analysis results of asphaltite samples are given in Figure 3-6. From the results obtained, it was determined that the asphaltite samples contained metals such as Ca, Si, Al, Fe, V, Ti, Ni, Mo as well as C, O, S.

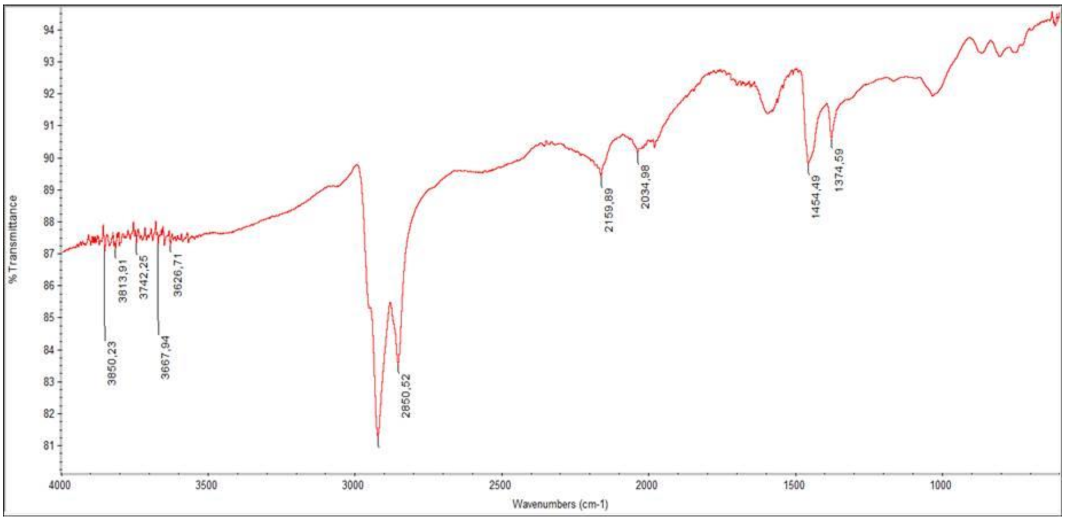

Figure 2. *FTIR analysis of Hakkari-1 sample*

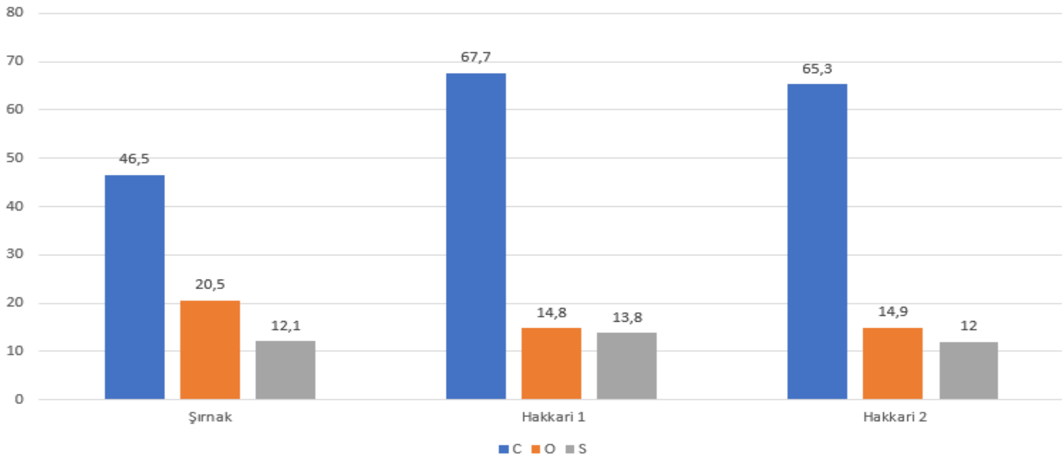

Figure 3. *XRF analysis results of Hakkari-1, 2 and Şırnak asphaltite samples (c, o, s)*

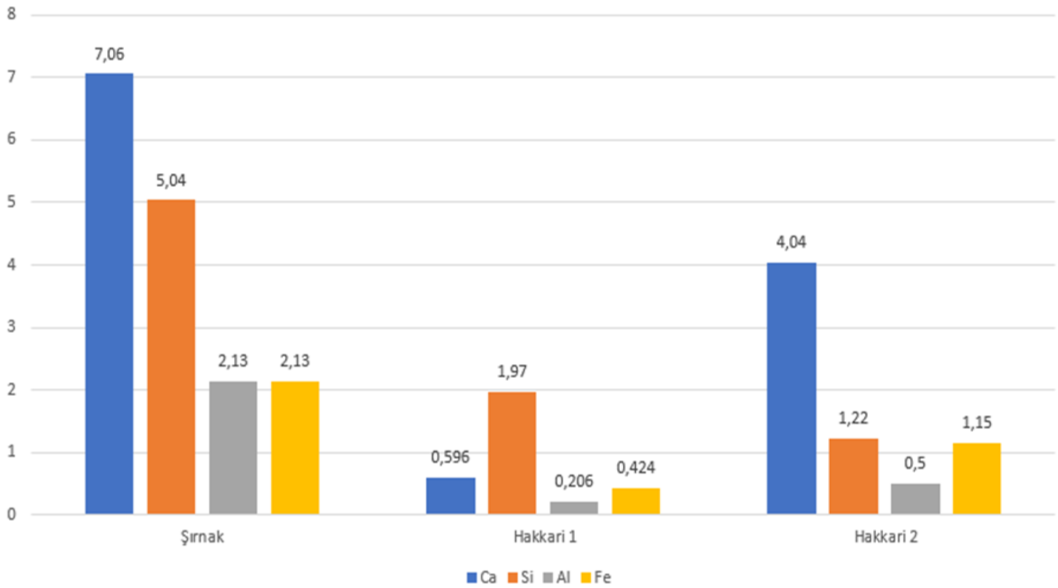

Figure 4. *XRF analysis results of Hakkari-1, 2 and Şırnak asphaltite samples (Ca, Si, Al, Fe)*

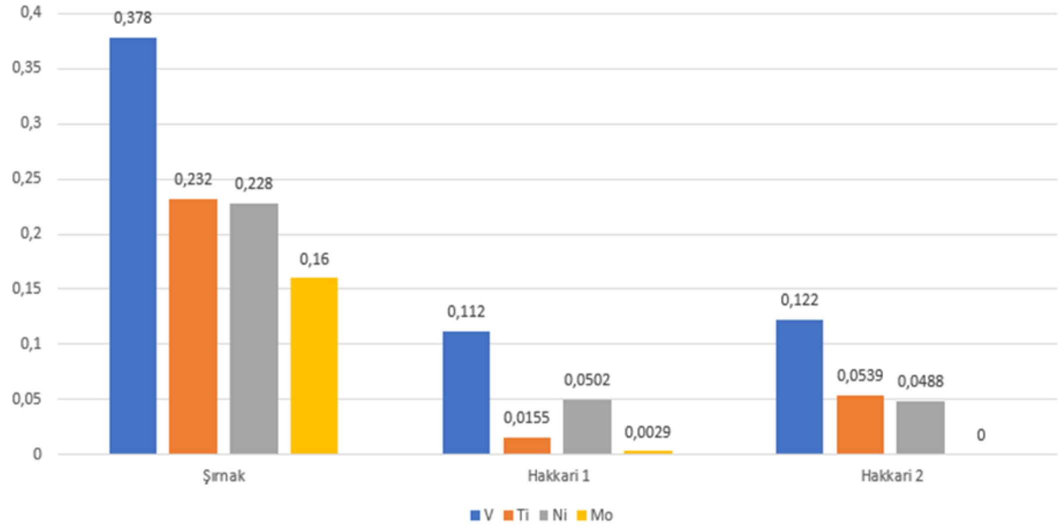

Figure 5. *XRF analysis results of Hakkari-1, 2 and Şırnak asphaltite samples (V, Ti, Ni, Mo)*

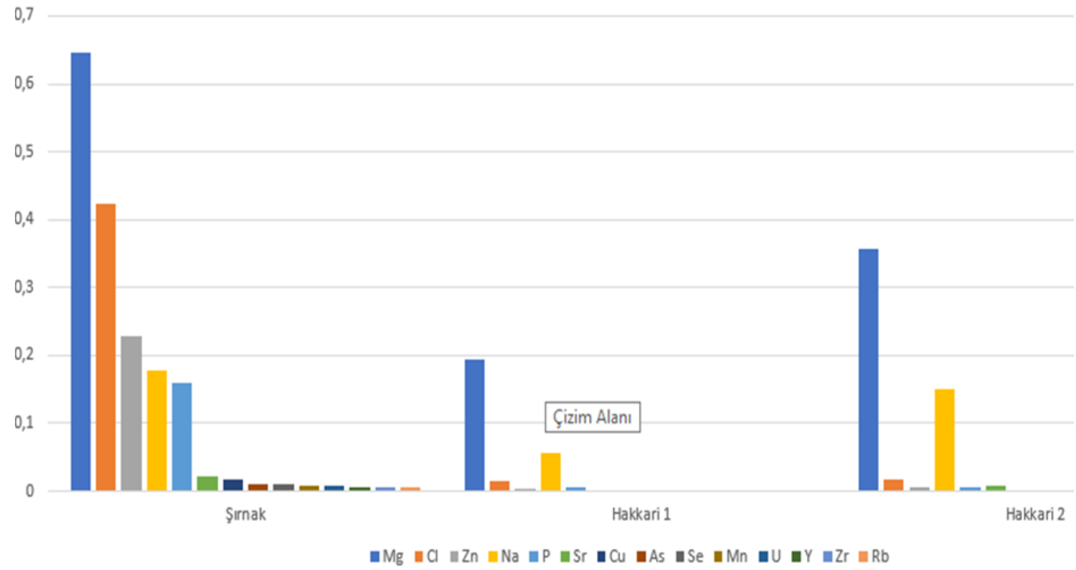

Figure 6. *XRF analysis results of Hakkari-1, 2 and Şırnak asphaltite samples (other content)*

According to the results of XRF analysis, the carbon ratios in Hakkari-1 and Hakkari-2 asphaltite samples (67.7% and 65.3%, respectively) are significantly higher than Şırnak asphaltite (46.5%) and the oxygen content is low. The high carbon content of Hakkari asphalt will allow the production of valuable liquid products with various hydrocarbon content (gasoline, diesel fuel, etc.) with higher efficiency under pyrolysis process conditions. In addition, under pyrolysis conditions, thermodynamically significant proportions of gas products such as H_2 and C_1-C_4 can be obtained. Whether liquid or gaseous products formed under pyrolysis conditions may contain unsaturated hydrocarbons as well as saturated hydrocarbons. If the process of pyrolysis of asphaltites is applied throughout the industry, the hydrocarbon products to be produced, especially the liquid products, must be purified from unsaturated hydrocarbons and sulfurous compounds by catalytic hydrogenation method. Although Şırnak asphthalite has a relatively low carbon ratio, it has a much higher metal ratio and metal diversity than Hakkari asphaltite.

This situation is thought to bring precious metals such as Al, Fe, K, V, Zn to the economy as well as other hydrocarbon products from Şırnak asphaltite throughout the industry. In addition, in the results of the analysis, it was concluded that both Şırnak and Hakkari asphaltites contain sulfurous compounds in high rates (approximately 12-14%). These sulfurous compounds are thought to be composed mainly of different thiophenes and mercaptans. Under pyrolysis conditions, these sulfurous compounds can deteriorate and turn into hydrogen sulfide and sulfur oxides, and elemental sulfur, which is widely used in different industrial areas, can be produced on their basis. As a result of the pyrolysis of asphaltites, heavy products that may consist mainly of polycyclic aromatic hydrocarbons (naphthalene, terphenyls, etc.) will be able to be used in bitumen and asphalt production and other industrial areas. The fact that Hakkari asphaltite has a higher carbon content, it is possible to acquire from Şırnak asphaltite more valuable liquid and gas products as fuels, chemicals, etc.

3.2. Pyrolysis Results of Asphaltite Samples

The pyrolysis of Hakkari and Şırnak asphaltite samples was investigated in nitrogen gas environment and without nitrogen using vaious temperature (350-700°C) and vacuum pressure (100-600 mmHg) and various asphaltite particle sizes (100-500 µm). In addition, the effect of different raw material feeding methods and commercial Al-Ni-Co catalyst on pyrolysis results was also examined in the experiments. One of the main goals targeted in the pyrolysis process was to determine the conditions under which high liquid product yield could be achieved.

GC-MS analysis methods were used for liquid product analysis obtained as a result of pyrolysis and FTIR analysis methods were used for solids. According to the experimental pyrolysis results obtained, it was observed that the increase in vacuum pressure and the decrease in asphaltite grain sizes increased the yield of the liquid product obtained. In addition, the realization of pyrolysis in nitrogen gas environment causes an increase in liquid and gas product yield. The use of catalyst and different raw material feeding methods in the process has less effect on product efficiency.

Process temperature has the most effect on the efficiency of liquid and gaseous products obtained in pyrolysis supply in asphaltite raw material. In Figure 7 below, the effect of pyrolysis temperature in the Hakkari-1 asphaltite sample is given to the yield of liquid, gas and solid products. Liquid product yield from Hakkari 2 and Şırnak samples is about 12 and 13 percent. It has been determined that under the continuous feeding conditions of the raw material, the liquid product yield increases significantly with the temperature increasing up to 700°C and in the batch system up to 550-650°C. In addition, the highest 16.5% liquid product yield was achieved at 700°C temperature, 400 mmHg vacuum pressure, 2g/min raw material feed rate and 500 µm particle size in continuous feeding conditions. The content of GC-MS analysis of the liquid product obtained under these conditions is given in Table 2 and its chromatogram in Figure 8.

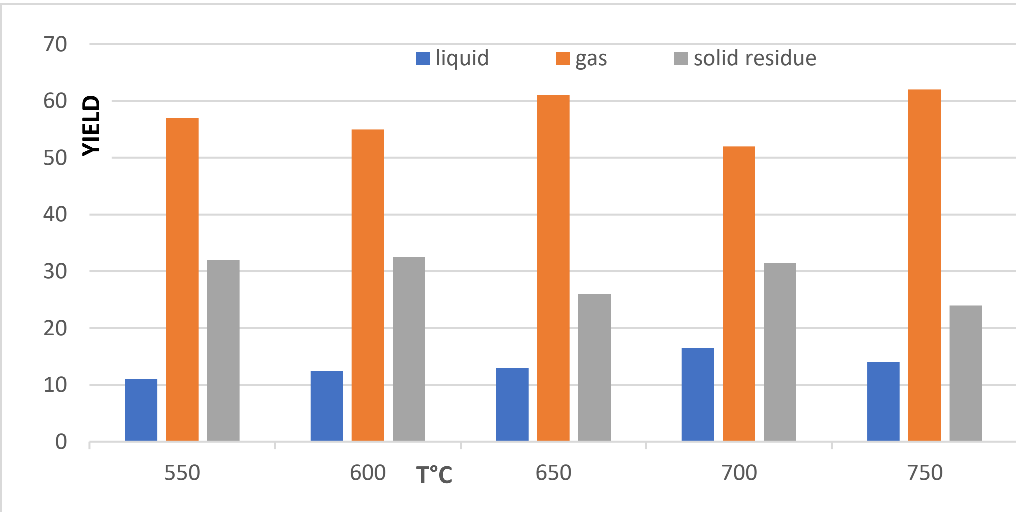

Figure 7. *The effect of pyrolysis temperature of Hakkari-1 asphaltite on liquid, gas and solid product yields*

As can be seen from Table 2 the liquid product mostly contains aliphatic hydrocarbons and their homologues. The carbon number of aliphatic hydrocarbons varies mainly in the C_8 (1-octane) and C_{20} (2,6,10,14-hexadescent) ranges. The aromatic compounds in the liquid are mainly composed of monocyclic (single-ring) and polycyclic (multi-ring) hydrocarbons. Single-ring aromatics mostly contain di-methyl benzenes (i.e. precious xylenes). Multi-cyclic aromatic hydrocarbons are mainly composed of naphthalene, biphenyl and their homologers. In addition, the liquid product contains a small amount of anthracene.

Table 2. *Components and percentages of liquid product GC-MS from the first experiment*

Detention time	component name	percent	Type	Detention time	component name	percent	Type
2,316	1-OCTENE	0,772	Alkene	12,395	Naphthalene, 2-methyl-	3,59	Polycyclic aromatic
2,725	1,3-Dimethyl-1-cyclohexen	0,126	Cycloalkene	12,607	Tridecane	0,982	Alkane
2,838	Cyclohexane, ethyl-	0,246	Alkane	14,263	Hexadecane, 2,6,10,14-tetramethyl	0,321	Alkane
3,237	Benzene, 1,3-dimethyl-	3,802	Aromatic	14,423	Benzo[b]thiophene, 3,5-dimethyl-	1,203	Sulphurous aromatic
3,362	p-Xylene	10,061	Aromatic	14,553	Naphthalene, 1-ethyl-	0,885	Polycyclic aromatic
3,487	Thiophene, 3,4-dimethyl-	0,302	Sulphurous aromatic	15,079	Naphthalene, 1,6-dimethyl-	1,016	Polycyclic aromatic
3,839	Nonane	0,835	Alkane	15,143	Naphthalene, 2,3-dimethyl-	0,679	Polycyclic aromatic
4,292	Benzene, (1-methylethyl)-	0,365	Aromatic	15,476	Naphthalene, 2,3-dimethyl-	0,379	Polycyclic aromatic
4,453	Octane, 2,6-dimethyl-	0,2	Alkane	15,661	Biphenylen	0,393	Polycyclic aromatic
4,846	Benzene, propyl-	1,03	Aromatic	15,793	Naphthalene, 1,4-dimethyl-	0,652	Polycyclic aromatic
5,009	Benzene, 1-ethyl-2-methyl-	4,771	Aromatic	16,819	Pentadecane	1,871	Alkane
5,143	Benzene, 1,2,3-trimethyl-	8,97	Aromatic	16,913	Benzo[b]thiophene, 2-ethyl-7-methyl-	0,566	Sulphurous aromatic
5,804	Decane	0,825	Alkane	17,336	Naphthalene, 1,4,5-trimethyl-	0,468	Polycyclic aromatic
6,557	Indane	0,515	Aromatic	17,649	Naphthalene, 1,6,7-trimethyl-	0,394	Polycyclic aromatic
6,746	Indene	0,916	Aromatic	17,965	Naphthalene, 1,4,6-trimethyl-	0,858	Polycyclic aromatic
6,925	Benzene, 1-methyl-3-propyl-	0,755	Aromatic	18,431	Naphthalene, 1,4,5-trimethyl-	0,466	Polycyclic aromatic
7,016	p-Mentha-1,5,8-triene	0,388	Cycloalkene	18,72	Hexadecane	1,259	Alkane
7,089	Benzene, 1-ethyl-2,4-dimethyl-	2,782	Aromatic	20,614	Heptadecane	1,41	Alkane
7,851	1-Undecene	0,471	Alkene	21,408	Dibenzothiophene	0,675	Sulphurous aromatic
8,049	Undecane	0,766	Alkane	21,879	Anthracene	0,683	Polycyclic aromatic
8,342	Benzene, 1,2,3,5-tetramethyl-	0,432	Aromatic	22,83	Octadecane	0,798	Alkane
8,478	Benzene, 1,2,4,5-tetramethyl	0,699	Aromatic	22,533	Hexadecane, 2,6,10,14-tetramethyl-	0,545	Alkane
8,899	1H-Indene, 2,3-dihydro-5-methyl-	0,284	Aromatic	23,142	Dibenzothiophene, 4-methyl-	1,246	Sulphurous aromatic
9,131	Benzene, (1-methyl-2-cyclopropen-1-yl)-	0,973	Aromatic	23,857	1-Methyldibenzothiophene	0,489	Sulphurous aromatic
9,207	Benzene, 1,2,3,4-tetramethyl-	0,624	Aromatic	23,927	Phenanthrene, 1-methyl-	0,348	Polycyclic aromatic
9,257	2-Methylindene	0,909	Aromatic	24,062	Nonadecane	0,678	Alkane
9,901	Naphthalene	1,511	Polycyclic aromatic	24,806	3,7-Dimethyldibenzothiophene	1,811	Sulphurous aromatic
10,099	Benzo[b]thiophene	0,296	Sulphurous aromatic	25,155	3,7-Dimethyldibenzothiophene	0,749	Sulphurous aromatic
10,16	1-Dodecene	0,391	Alkene	25,665	Eicosane	0,745	Alkane
10,354	Dodecane	0,723	Alkane	27,209	Heneicosane	1,15	Alkane

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Based on the GC-MS results, the total proportion of hydrocarbons detected in the liquid product of asphaltite pyrolysis was 73% and 27% was not detected by GC-MS method. The classification of hydrocarbons according to the results of the analysis is as follows. In each hydrocarbon group, the percentage of the total proportion belonging to that class is given. Alkane 13.35 %, Alkene 1.63 %, Cycloalkene 0.51 %, Aromatic 37.8 %, Polycyclic aromatic 12.32 %, Sulphurous aromatic 7.33 % As can be seen from the above results, approximately 50% of the hydrocarbons detected in liquid products are monocyclic aromatic compounds, that is, they consist of benzol and mainly precious alkyl benzols. Therefore, it is economically important to extract and evaluate these valuable hydrocarbons from the liquid products obtained from the asphaltite pyrolysis method by the extraction method.

In order to recover the hydrocarbons remaining after the extraction of aromatic hydrocarbons, they all need to be subjected to the combined catalytic hydrocleaning method. As a result of this method, the double bonds of all unsaturated hydrocarbons are saturated with hydrogen, and sulfurous compounds will be converted into hydrocarbons and hydrogen sulfide as hydrocracking. The resulting 15% alkanes and cycloalkanes can be used as fuel. Naphthalene and alkylnaphthalenes can be used as valuable chemicals in the petrochemical industry and other industrial areas. From the hydrogen sulfide formed, elemental sulfur and hydrogen can be obtained by certain methods in industry.

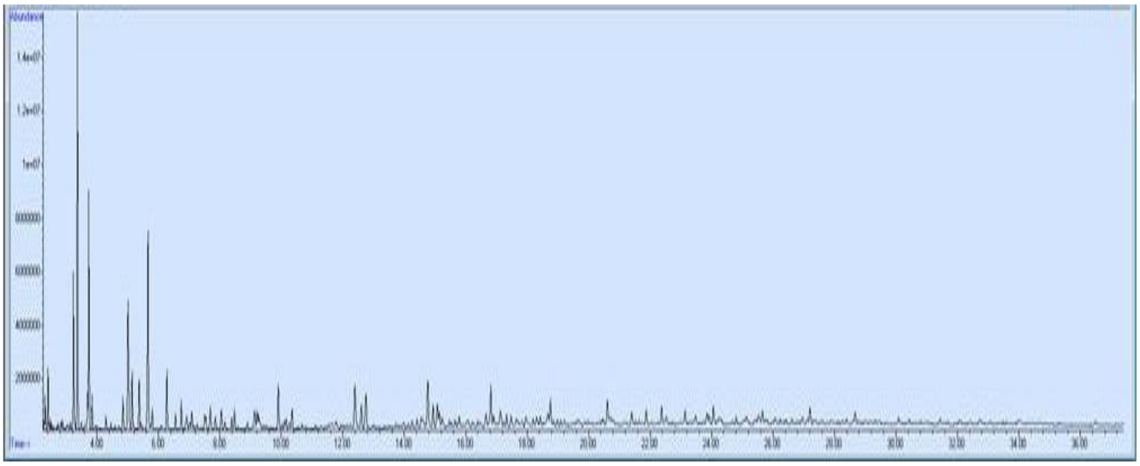

Figure 8. *GC-MS chromatogram of the first plant*

It is evident from the GC-MS analysis results of liquid products obtained at different pyrolysis temperatures that the change in pyrolysis temperature in the range of 500-700°C affects their concentration more than the hydrocarbon content of the obtained liquid products. The liquid product obtained in pyrolysis of Şırnak asphaltite with the use of Al-Ni-Co catalyst contains alkanes and aromatic hydrocarbons, as well as various cyclic alkanes (naphthens) such as cyclo-pentane, cyclo-hexane etc. in a significant amount. Sulfurous compounds in liquid products are mostly composed of thiofene homologs (benzo-thiophene, etc.).

4. CONCLUSION

Based on the experimental data obtained and the results of various physical and chemical analyzes, it can be said that asphalides, which have large reserves in our country, have a very rich and diverse hydrocarbon content (mainly saturated aliphatic and aromatic hydrocarbons) as a petroleum-based material. In addition, as research shows, asphthalites also contain high amounts of organic sulfurous compounds, mostly thiophene-based. Therefore, with the use of effective technological and environmentalist methods, it is important both economically and strategically to transform asphaltites into valuable products to constribute to our country's industry. Taking these into account, different technological methods and recommendations that can be applied in industry for the effective evaluation of asphaltites, as well as thermal pyrolysis:

1. Catalytic Hydrocracking

Asphthalates can be subjected to Catalytic Hydrocracking process with a high pressure of 200-250 bar hydrogen pressure and low temperature 300-350°C. In this process, all heavy hydrocarbons, aromatics and sulfurous compounds are broken down by exposure to hydrocracking reactions, resulting in sulfur-free gasoline, diesel fuel C_1-C_4 (Methane, ethane, propane, butane) and Hydrogen sulfide (H_2S). In addition, from the formed hydrogen sulfide, elemental sulfur, which is widely used in industry, can be produced. Industrial catalysts can be used in the process.

2. Extraction

Fractions containing monocyclic aromatic hydrocarbons (benzol and alkylbenzols) and cyclic aromatic hydrocarbons (naphthalene and alkylnaphthalenes) contained in asphaltites are separated under vacuum and precious pure aromatic hydrocarbons can be obtained from them by extraction (removing valuable aromatics with a solvent by distillation method). The solvent is constantly circulating in the system. The rest of the asphaltite can be subjected to Catalytic Hydrocracking to obtain liquid products such as gasoline, diesel fuel and C_1-C_4 gas products that can be used as fuel.

3. Hydrodealkylation-hydrocracking

The only difference of this method from method 2 is that the aromatic fractions separated from the asphaltite are subjected to the high-temperature and low-pressure hydrodealkylation-hydrocracking process instead of extraction, and finally pure benzol and naphthalene can be obtained. In this process, alkyl benzons are subjected to the dealkylation reaction and turn into a very important hydrocarbon such as benzol in the petrochemical industry. The remaining non-aromatic ones also turn into gases as hydrocracking. Thus, as a result of the high-temperature hydrodealkylation-hydrocracking process, high-purity benzol (99,99%) and the gas products C_1-C_4 are obtained. The hydrodealmulation-hydrocarbon process is carried out catalytically at a hydroreal pressure of 625°C and 55-60 bar and thermally at a hydrogen pressure of 700-725°C and 25-30 bar. Each of these proposed methods has its advantages and flaws. Therefore, of course, in order to determine an optimal production method, it is necessary to make a preliminary feasibility of their economic and technological indicators. It is also important that the selected technology is tested on a pilot scale before its industrial application.

ACKNOWLEDGEMENT

We would like to thank Gazi University BAP unit for its support in the research project FDK-2022-7294 throughout this study.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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