

Co-liquefaction Behaviour of Elbistan Lignite and Olive Bagasse

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Abstract. In the present study, co-liquefaction potential of Elbistan lignite and Balikesir olive bagasse were investigated by direct coal liquefaction process. The olive bagasse is a cheap and abundant biomass, so it is used to decrease the cost of oil production from the lignite. The effect of blending ratio of the lignite and the olive bagasse on liquefaction conversion and oil yield were investigated. Characterization studies of the starting materials were done using XRD, FTIR, DTA/TG and elemental analysis. Elemental compositions of liquefaction products were also determined and the composition of the obtained oil was identified by GC/MS. DTA and TGA results indicated the synergistic effect of the lignite and the olive bagasse and maximum oil conversion (36 %) was obtained from 1:3 blending ratio of lignite: olive bagasse. The results showed that the obtained oil was paraffinic-low waxy oil with 22.5 MJ/kg of calorific value and 0.95 g/cm³ density.

1. Introduction

Elbistan lignite is used in Afsin-Elbistan thermal power plant as a fuel due to its low calorific value and high ash content. However, the lignite should not be burnt directly because it causes environmental pollution. While providing the demand for energy which is rising depending on industrialization, the environment should be protected as well. Turkey is one of the countries which has limited oil and abundant lignite reserves (its 46 % in Afsin-Elbistan region) [1], so researches must be done to find alternative oil production methods in the near future, even though the oil prices have remained low recently.

Liquefaction is one of the clean energy production way from coal [2, 3] and direct liquefaction technique will become a viable option for the production of transportation fuels in the early part of the next century [4]. However, the liquefaction process is very expensive, so recently, biomasses, which are locally available, cheap and renewable energy sources, have been used to decrease the cost of the process and to provide more hydrogen into system. In addition, literature survey shows that co-liquefaction of coal and biomass increases the yield of oil production [2, 3]. In the present study, co-liquefaction properties of the Elbistan lignite and olive bagasse were investigated in detail.

The olive bagasse was used to increase the yield of oil production and to decrease the cost of liquefaction process and to supply more hydrogen, since the olive bagasse is cheap and abundant. 1,800,000 tonnes of olives are produced in Turkey and 35 - 45 kg per tonne olive mass is obtained every year [5].



2. Materials and methods

2.1. Starting samples

The lignite was taken from Afsin-Elbistan, Turkey and the olive bagasse was brought from Marmara Birlik Company, Balikesir, Turkey. The samples were crushed, ground and sieved. The sizes of the starting materials were selected as -20 mesh + 14 mesh in terms of our preliminary investigation.

2.2. Co-liquefaction setup and procedure

Direct coal liquefaction experiments were carried out in a 500 mL stainless-steel, automatic stirred autoclave. For each experiment, 30 g of the lignite and lignite olive bagasse mixture and 90 mL of tetralin without any catalyst were charged into the autoclave and closed the system. The system pressure was adjusted as 20 bar by N₂. The autoclave was heated for an indicated temperature (400 °C) at 60 min. After that, the autoclave was put into an ice-water bath to cool the system to room temperature. The soxhlet solvent extraction and evaporator system were used to separate the liquefaction mixture. The liquefaction products, char, asphaltene, preasphaltene and oil were obtained by following the literature data [6]. The blending ratio of the lignite: the olive bagasse was selected as 1:1, 2:1, 3:1, 1:2 and 1:3. The yield of the liquefaction products was calculated from mass balance equations.

2.3. Characterization of the samples and liquefaction products

Characterization and determining chemical structure of the starting materials was performed by using Rigaku Miniflex 600 with Cu K α (40 kV, 15 mA, λ =1.54050 Å) XRD, Perkin Elmer Spectrum One FTIR, CHNS Elemental analyzer device (Leco CHNS 932, LECO Corporation, St. Joseph, MI), Shimadzu TGA and DTA-50, 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).

3. Results and discussions

In the coal liquefaction process, coal is generally mixed with biomass, having high hydrogen content in order to increase the oil yield. The main idea is to create synergism effect between coal and biomass which can be used as a hydrogen donor for the system [7]. Therefore, elemental compositions of starting materials were determined and the results are given in Table 1. It could be seen that the olive bagasse had higher carbon and hydrogen content than the lignite, indicating that the olive bagasse may cause synergism effect and increase the oil yield. In addition, the olive bagasse had a low sulphur content and high calorific value of 4553 Kcal/kg.

Table 1. Proximate and ultimate analysis of the lignite and olive bagasse

Sample	Proximate analysis (%)				Elemental analysis (%)				
	M	A	V	FC	C	H	N	S	O*
Elbistan lignite	4.99	38.08	35.09	21.84	28.08	3.483	1.035	3.552	63.85
Olive bagasse	7.49	3.3	53.26	75.95	47.82	6.032	1.961	0.147	44.04

* By difference.

The XRD patterns of the starting materials are given in figure 1a. It can be seen that the olive bagasse had an amorphous structure and prolate curve between 15° and 25° 2 θ values indicated the lignocellulosic structure [8]. The XRD pattern of the lignite showed that the wide peak between 10° and 20° 2 θ values represented the aromatic carbon and heterogeneous structure consisting of quartz, gypsum, pyrite, dolomite and calcium silicate. IR spectra belonging to the lignite are given in figure 1b. The broad and wide band indicated the hydroxyl groups in water. The bands at 2952 cm⁻¹ and 2882 cm⁻¹ represent the aliphatic hydrocarbons and the bands at 1600 cm⁻¹ and 1400 cm⁻¹ indicate C=C and C=O olefin vibration in aromatic structure. The strong band at 1019 cm⁻¹ show Si-O and C-O vibration and the bands between 900 cm⁻¹ and 700 cm⁻¹ wave numbers belong to the C-H aromatic compounds. The

IR spectrum of the olive bagasse indicates the bands: 3500 cm^{-1} associated with OH, 2900 cm^{-1} associated with $\nu(\text{CH}_2)$ vibration, 1600 cm^{-1} associated with $\nu(\text{C}=\text{C})$ bands, 1540 cm^{-1} associated with $\text{C}=\text{O}$ vibration. The other bands generally represent the aromatic structure [9]. Thermogravimetric curve in figure 1c proved that the weight loss of the mixture of the lignite and the olive bagasse was higher than that of the lignite, meaning easy decomposition of weak molecular structure of the olive bagasse while it decomposes depending on temperature, free radicals or intermediary products that react with coal and synergetic effect occurs in the system [10]. DTA curves of the lignite and the mixture are given in figure 1d. It can be seen that the new peaks occurred at 411°C , 444°C and 700°C . This showed the decomposition of carbonate compounds in the lignite structure due to the low thermal decomposition properties of olive bagasse, showing the synergetic effect [6, 7].

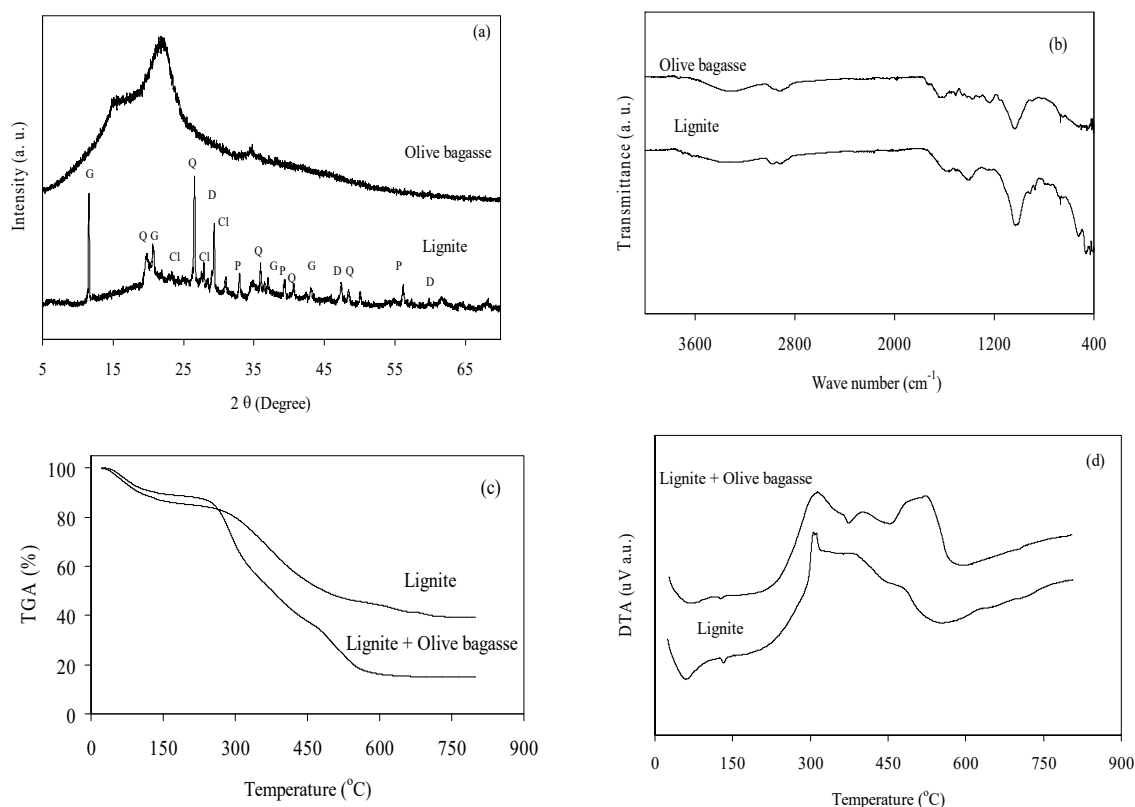


Figure 1. Characterization of the starting samples, a) XRD pattern, b) FTIR spectra, c) TGA curves and d) DTA curves

The product distributions during liquefaction of the Elbistan lignite and co-liquefaction of the Elbistan lignite and the olive bagasse are given in figure 2. It can be observed that with increasing the olive bagasse amount in the mixture, the total conversion, preasphaltene, asphaltene and oil yield increased, while carbon yield decreased. The results proved the synergism effect between the lignite and the olive bagasse. The oil conversion difference increased from 24 % to 36 % of 1:3 blending ratio of the lignite: the olive bagasse. The elemental analysis of all the products was also done (Table 2), indicating that the carbon content increased from char to oil and especially lower sulphur content was obtained for 1:3 blending ratio of the lignite: the olive bagasse, which is a good point for environment. In addition, the oxygen content was lower than 6 %, which is an important property of phytogenetic fuel [3].

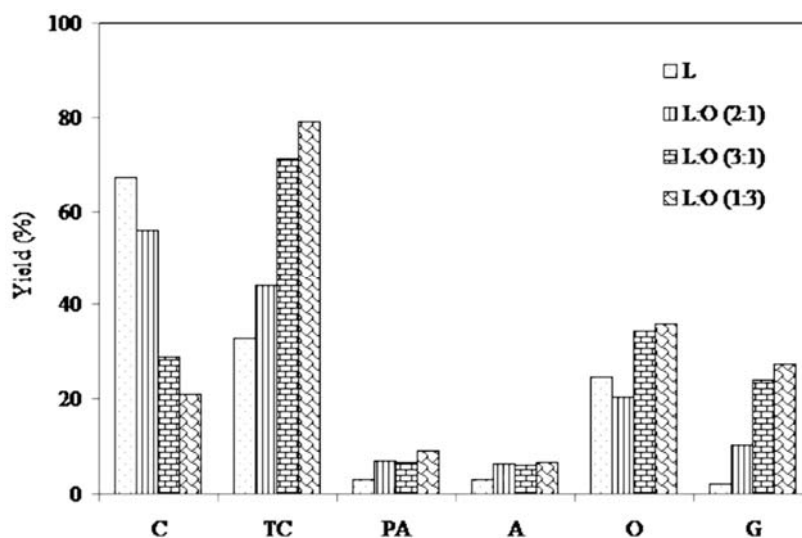


Figure 2. Product distribution and comparison of the blending ratio of the product yields. C: char, TC: total conversion, PA: preasphaltene, A: asphaltene, O: oil and G: gas

Table 2. Elemental analysis of the liquefaction of lignite and lignite + olive bagasse mixture

Sample		Elemental analysis (daf). wt %				
		C	H	N	S	O*
Elbistan lignite	Char	14.98	1.59	0.74	2.30	80.40
	Preasphaltene	72.67	5.78	2.50	1.84	17.20
	Asphaltene	79.13	7.06	1.71	2.01	10.09
	Oil	85.72	8.659	0.216	0.287	5.12
The mixture	Char	17.01	1.771	0.46	2.085	78.67
	Preasphaltene	75.20	5.82	1.74	0.40	16.84
	Asphaltene	81.06	6.74	0.74	0.54	10.92
	Oil	87.21	8.81	0.86	0.33	2.79025

* By difference.

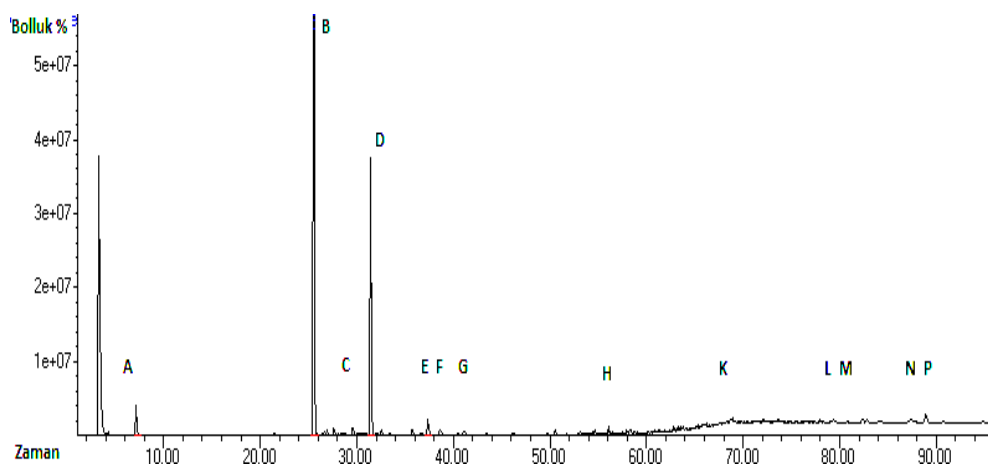


Figure 3. Mass chromatogram of the co-liquefaction oil product

The components inside the oil and its chemical structure were determined by GC-MS analysis. Mass chromatogram of the co-liquefaction oil product (the blending ratio 1:3 of the lignite: the olive bagasse) and components detected by GC-MS are given in figure 3 and Table 3, respectively. The results indicated that the oil structure generally composed of naphthalene, followed by phenolic compounds. In terms of the distribution of light (C_{1-5}), medium (C_{6-14}) and heavy hydrocarbons (C_{15+}), the mixture of the Elbistan lignite and the olive bagasse generated paraffinic-low waxy oil [11]. The calorific value and density of the obtained oil were found as 22.5 MJ/kg and 0.95 g/cm³

Table 3. Components detected by GC-MS

Peak Code	Retention time (min)	Probable compound	Molecular formula	Abundance, %
A	7.169	Toluene	C ₇ H ₈	1.91
B	25.565	Naphthalene. 1.2.3.4-tetrahydro.	C ₁₀ H ₁₂	46.08
C	29.565	Naphthalene. 1-ethyl-1.2.3.4-	C ₁₂ H ₁₆	0.62
D	31.379	Naphthalene	C ₁₀ H ₈	22.28
E	37.353	Naphthalene. 2-methyl	C ₁₁ H ₁₀	1.40
F	38.583	Butylated Hidroxytoluene	C ₁₅ H ₂₄ O	0.70
G	41.118	Naphthalene. 1-methyl	C ₁₁ H ₁₀	0.49
H	56.069	1-Naphthalenone. 1.2.3.4-	C ₁₀ H ₁₂ O	0.61
K	68.892	1.2-Dihydro-7.12-	C ₂₀ H ₁₆	2.54

4. Conclusions

Thermogravimetric and elemental analysis of the starting materials show that there is synergistic effect in the co-liquefaction of Elbistan lignite and the olive bagasse. The olive bagasse promotes the thermal decomposition of the lignite and gives more hydrogen into the system. The highest oil yield was obtained with 1:3 blending ration of the Elbistan lignite and the olive bagasse. The co-liquefaction process generated paraffinic-low waxy oil with 22.5 MJ/kg calorific value.

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