# Liquefaction Potential of Adiyaman Peat

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**Abstract**. In the present study, liquefaction potential of Adiyaman peat was studied by direct liquefaction technique to obtain oil as a fuel purposes due to its high carbon and hydrogen content and low sulphur ratio. The peat and liquefaction products, named char, asphaltene, preasphaltene and oil, were characterized by XRD, FTIR, SEM, DTA/TG and elemental analysis. The compositions of the obtained oil were also identified by GC/MS. The results indicated that the obtained oil was paraffinic-low waxy oil with 21.73 MJ/kg of calorific value and 0.93 $g/cm^3$ density and it was composed of naphthalene and phenolic groups. The oil conversion ratio was found to be 29 %.

## 1. Introduction

Peat comprises of natural atrophy and incomplete disintegration of dead plants and it is counted the first stage of coalification. Due to its lower ash content and its cost compared to some other fossil fuels, it has many economic benefits to be used as a fuel [1, 2]. Therefore, peat was put into a catalogue of renewable natural energy sources by European Parliament [3]. In addition, peat is taken into account as biomass feed stock due to its aliphatic and aromatic structures, so biofuels (CO, $H_2$, $CH_4$) can be produced from peat by pyrolysis, gasification or other bio-refining technologies [4]. In the literature, there are some studies on pyrolysis and gasification process of peat and peat mixture with coal [5, 6]. On the contrary, liquefaction property of peat has not been fully researched yet, so it is a promising study on liquefaction properties of peat.

In the present investigation, liquefaction properties of Adiyaman peat were studied and the obtained products were characterized for the first time in the literature. In the liquefaction process, conventional direct coal liquefaction process was followed. Adiyaman peat was selected as a source for liquefaction process, since Adiyaman has a huge peat reserve and high carbon and hydrogen content and low sulphur ratio, indicating that it is a cheap and abundant and renewable energy source.

## 2. Materials and methods

### 2.1. Liquefaction setup and procedure

Peat liquefaction experiment was done using a 500 mL stainless-steel, automatic stirred autoclave. Peat sample (30 g) and tetralin (90 mL) without any catalyst were charged into the autoclave and then system pressure was adjusted as 20 bar by $N_2$. The autoclave was heated for an indicated temperature (400 °C) at 60 min. Then 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, namely char, asphaltene, preasphaltene and oil were

obtained by following the literature data and the yield of the liquefaction products were calculated from mass balance equations [7].

*2.2. Characterization of the peat and liquefaction products*

The phase compositions of the peat and the liquefaction products were analyzed by X-ray powder diffraction and the patterns were recorded using Rigaku Miniflex 600 with Cu Kα (40 kV, 15 mA, λ=1.54050 Å). The vibrational modes of functional groups of the peat and the obtained products were defined by Perkin Elmer Spectrum One FTIR. The morphology as well as the chemical structure of peat was investigated using LeO EVO 40 scanning electron microscope. Thermal behaviour of the peat was analyzed by Shimadzu TGA. Elemental analysis of the peat and the products were done by CHNS Elemental analyser device (Leco CHNS 932, LECO Corporation, St. Joseph, MI). In addition, the oil was characterized by 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

The XRD pattern of the peat is given in figure 1a. It can be seen that the peat had amorphous structure and wide curve between 15 ° and 25 ° 2 θ values indicated the lignocellulose materials [8]. The IR spectrum of the peat indicates the bands: 3500 cm$^{-1}$ associated with OH, 2900 cm$^{-1}$ associated with $\nu_{as}(CH_2)$ vibration, 1600 cm$^{-1}$ associated with $\nu(C=C)$ bands, 1540 cm$^{-1}$ associated with C=O vibration. The other bands generally represent the aromatic structure [9].
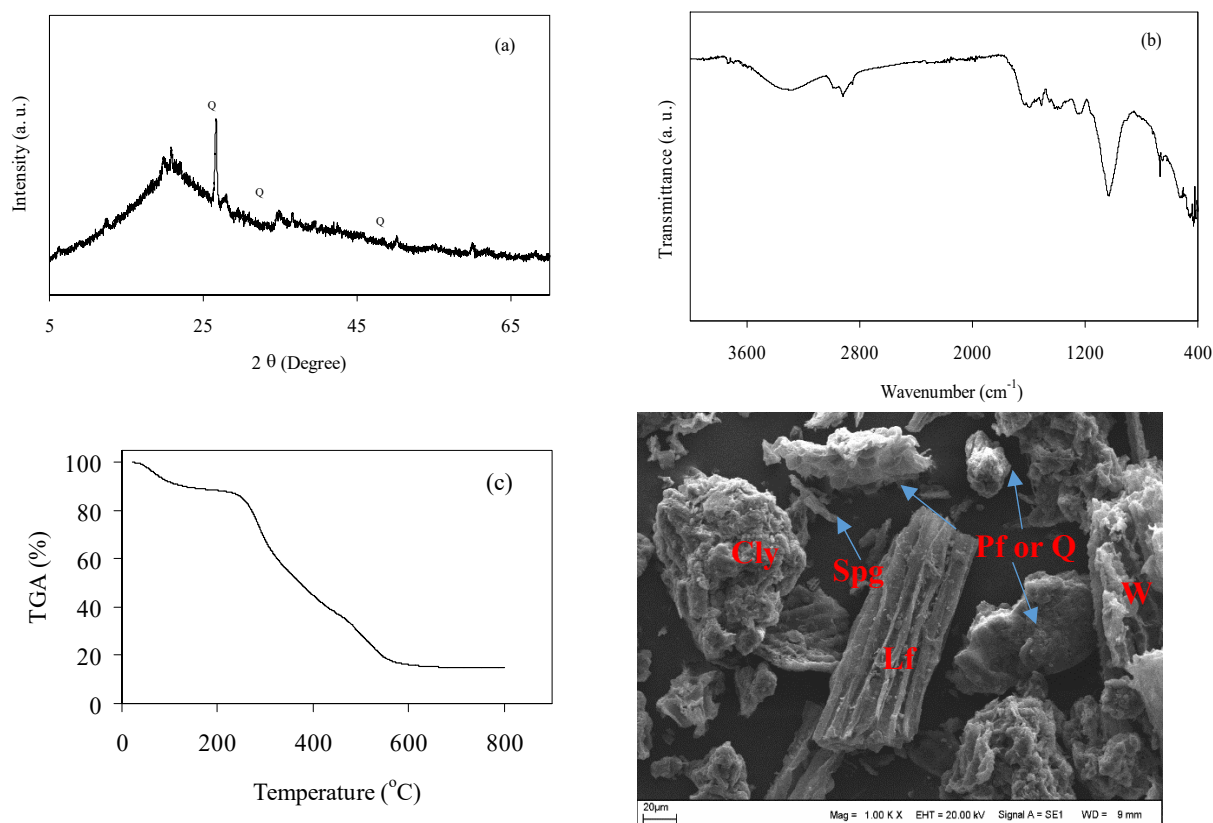


**Figure 1.** Characterization of the peat, a) XRD pattern, b) FTIR spectra, c) TGA curves and d) SEM

Thermogravimetric curve in figure 1c showed easy decomposition of the peat, representing the weak molecular structure. The main components of the peat include a wood (W: roots and parts of trees), a leaf fragment with stomata (Lf), spicules of fresh-water sponges (Spg) and a potassium feldspar or quartz, seen on SEM image in figure 1d [10, 11]. The results showed that peat structure mainly consists of hemi-cellulose, cellulose and lignin [12], meaning that it has a high carbon content. To support this, elemental and ultimate analysis was also done and the data are given in Table 1. In terms of the elemental composition (C<53, 5.0<H<6.1), the peat can be classified as low decompose peat type [13].

**Table 1.** Proximate and ultimate analysis of the peat

| Proximate analysis (%) | | | | Elemental analysis (%) | | | | |
|---|---|---|---|---|---|---|---|---|
| M | A | V | FC | C | H | N | S | O* |
| 4.79 | 21.29 | 32.82 | 41.1 | 42.93 | 5.23 | 2.101 | 0.32 | 49.43 |

* By difference.

The product distributions during liquefaction of the different size of peat are given in figure 2. It can be seen that the yield of the liquefaction products showed particle size (P1: -20 mesh +35 mesh, P2: -35 mesh +70 mesh, P3: -70 mesh +100 mesh and P4: -100 mesh) independent character. The main goal of the present study is to obtain oil and Fig. 2 indicated that the oil conversion ratio was found to be 29 %, which is higher than that of some lignite reported in the literature [14, 15].
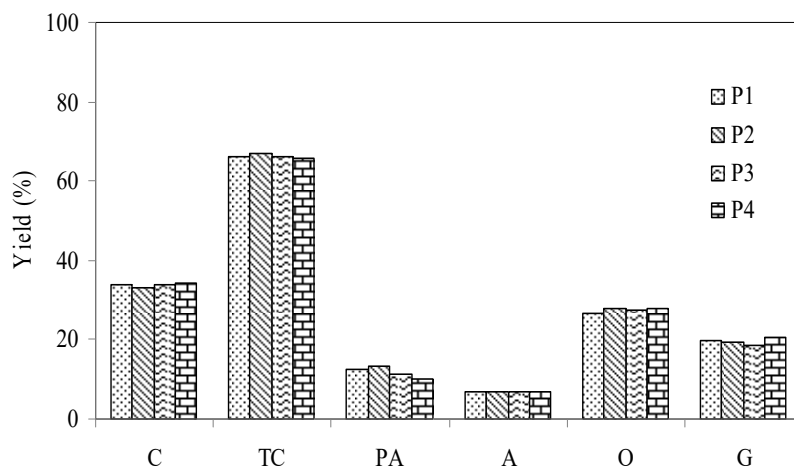


**Figure 2.** Product distributions during liquefaction of the different size of peat. C: char, TC: total conversion, PA: preasphaltene, A: asphaltene, O: oil and G: gas

The components inside the oil and its chemical structure were determined by GC-MS analysis. The results showed that there is no particle size effect on the oil structure and composition, so one mass chromatogram of the liquefaction oil product (figure 3) and one identification of components detected by GC–MS (Table 2) are given in the present study. The results indicated that the oil structure generally consisted of naphthalene, followed by phenolic compounds and the calorific value and density of the obtained oil were found as 21.73 MJ/kg and 0.93 g/cm$^3$.
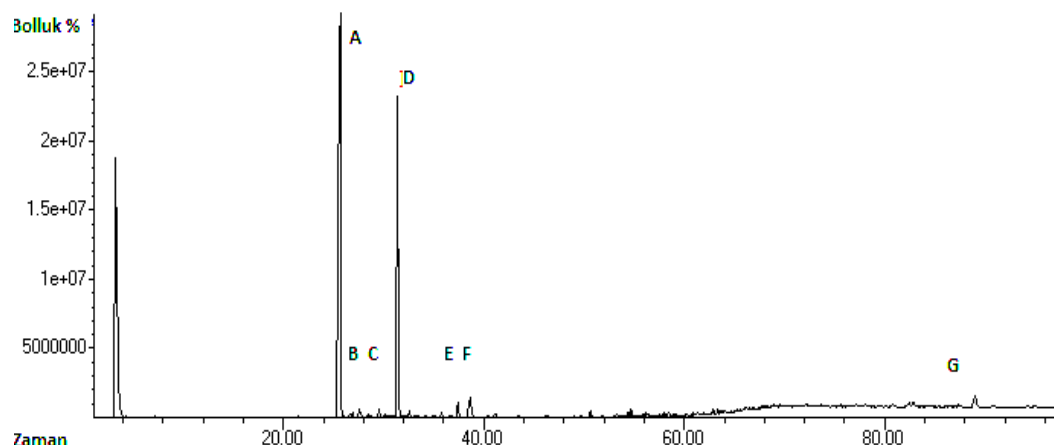
**Figure 3.** Mass chromatogram of the co-liquefaction oil product

**Table 2**. Components detected by GC–MS

| Peak | Retention time (min) | Name | Abundance, % |
|------|------|------|------|
| A | 25.571 | Naphthalene, 1,2,3,4-tetrahydro | 42.40 |
| B | 27.620 | Naphthalene, 1,2-dihydro | 0.55 |
| C | 29.588 | Naphthalene, 1-ethyl-1,2,3,4-tetrahydro | 0.75 |
| D | 31.396 | Naphthalene | 21.84 |
| E | 32.581 | Naphthalene, 1,2,3,4-tetrahydro-1-propyl | 0.60 |
| F | 35.773 | Naphthalene, 2-methyl | 1.02 |
| G | 88.971 | 2,2-Binaphthalene, 1,1,2,2,3,3,4,4-octahydro | 1.81 |

The other liquefaction products were characterized by XRD, FTIR and elemental analysis methods. The XRD patterns indicated that the char had a crystal structure and main component was quartz. This result supported the XRD and SEM results. In addition, the detected wide peak at 25 ° 2 θ represented amorphous carbon [16]. The XRD patterns (figure 4.a) belonging to asphaltene and preasphaltene showed the amorphous structure and it may be thought that the wide peak between the 10° and 30° represented to carbon structure. To support this inference, the elemental analyses were done and data are given in Table 3. It can be seen that the asphaltene and the preasphaltene had higher carbon content.

**Table 3.** Proximate analysis of the peat liquefaction products

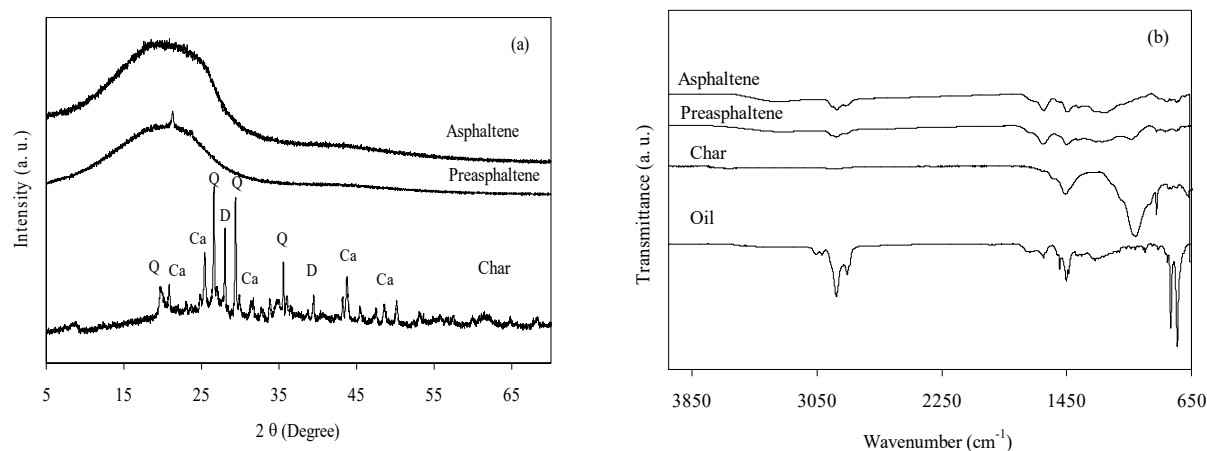| Sample | %C | %H | %N | %S | %O[*] |
|--------|------|------|------|------|------|
| Char | 21.72 | 1.827 | 1.005 | 1.018 | 74.43 |
| Asphaltene | 80.00 | 7.47 | 3.01 | 0.12 | 9.41 |
| Preasphaltene | 76.54 | 6.033 | 3.158 | 0.135 | 14.13 |
| Oil | 87.11 | 8.81 | 0.86 | 0.31 | 2.91 |

* By difference.

**Figure 4.** Characterization of the starting samples, a) XRD pattern, b) FTIR spectra

The FTIR spectrum (figure 4.b) of the char indicated the five main bands: 2900 cm$^{-1}$ associated with $\nu_{as}(CH_2)$ vibration belonging to alkenes, 1600 cm$^{-1}$ associated $\nu(C=C)$ vibration belonging to olefin, 1500 cm$^{-1}$ associated with aromatic and benzene rings, indicating that carbon - carbon structure in main peat and aromatic structure increased in the liquefaction products [9]. In addition, the FTIR spectra of the oil, asphaltene and preasphaltene indicated that the main structure consisted of C - C and C - O bonds, also demonstrated with the elemental analysis results.

## 4. Conclusions

The overall results indicated that Adiyaman peat had a great liquefaction potential and gave a good oil yield. The obtained oil was paraffinic-low waxy oil with 21.73 MJ/kg of calorific value and 0.93 g/cm$^3$ density and it was composed of naphthalene and phenolic groups. The oil conversion ratio was found as 29 %. In addition, it was found that the yield of the liquefaction products showed particle size independent character and the present study showed that Adiyaman peat might be evaluated as a source to obtain bio-oil by conventional direct liquefaction process.

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