Effects of Process Parameters on the Co-Liquefaction of Elbistan Lignite and Apricot Kernel Shell

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Abstract. In this study, the co-liquefaction of Elbistan lignite and biomass investigated by using apricot kernel shell as a biomass type. The liquefaction experiments were carried out under inert atmosphere and non-catalytic conditions. The effect of particle size, coal/biomass ratio, and reaction temperature were examined as a process variable to determine the effect of process parameters on total conversion of products obtained by liquefaction and the conversion of liquefaction products.

1. Introduction
Since it is causing environmental pollution and not economic, direct use of coal with high ash and sulfur content is not preferable. Before such fuels are used, the ash and sulfur ratios can be reduced to a certain amount or an alternative fuel can be obtained by liquefying the fuel. Usage of biomass as an energy resource alternative to petroleum is a topic of investigation today since it is renewable and does not cause environmental pollution. Use of biomass as diverse raw materials like plants, household wastes, animal wastes and microorganisms is considered to be a potential resource for energy generation. The apricot seed shell is thought to be a useful biomass source for the liquefaction process, due to the relatively small amount of ash and moisture contained therein. Various processes are being applied to convert biomass resources into a fuel effectively alternative to the petroleum. Some of these processes are gasification, liquefaction, supercritical gas extraction and pyrolysis. However, the most preferable method for generating a fuel direct alternative to petroleum is liquefaction [1, 2]. Coal conversion and coal liquefaction products (preasphaltene, asphaltene and oils) are obtained at different rates by applying various methods in the coal liquefaction studies. After the liquefaction, products are obtained in solid, liquid and gaseous forms. The efficiency of solid products (char) is an important parameter in determining the efficiency of liquid and gaseous products [3].

2. Experimental Section

2.1. Materials
During the liquefaction experiments, tetralin (98%, Sigma Aldrich), nitrogen gas (N₂ gas) and tetrahydrofuran (THF) (Merck) was used as the consumption material and a stirring and heating, batch reactor (Parr, 500 ml) was used.
2.2. Procedure

In this study, the effect of biomass particle size, reaction temperature and coal/biomass ratio on the liquefaction efficiency investigated by directly using liquefaction method in liquefaction experiments. The coal particle size, the initial pressure, and the solid/solvent ratio were fixed and the liquefaction process was be carried out in inert atmosphere and non-catalytic conditions. The liquefaction experiments conditions are given in Table 1. Only the optimum parameters of the liquefaction of Elbistan lignite available in the literature. The optimum biomass liquefaction parameters by the liquid product efficiency was defined after the experiments made only with the apricot seed shell and the solvent in 1:3 ratios. The optimum parameters in the liquefaction of coal and liquefaction of the biomass was taken as a base; and the experiment conditions to be made for the optimization of conditions in the joint liquefaction of the biomass and coal was determined. Analysis of the lignite and biomass samples were given in Table 2 and 3, flow chart of classification of the liquefaction products was shown in Figure 1.

Table 1. The liquefaction experiments conditions.

| Exp. no | Apricot kernel shell (g) | E. Lignite (g) | Temp (°C) | Time (min.) |
|---------|--------------------------|----------------|-----------|-------------|
| 1       | 30.0013                  | -              | 325       | 60          |
| 2       | 30.0003                  | -              | 350       | 60          |
| 3       | 30.0004                  | -              | 375       | 60          |
| 4       | 30.0001                  | -              | 390       | 60          |
| 5       | 15.001                   | 15.001         | 350       | 60          |
| 6       | 15.005                   | 15.005         | 375       | 60          |
| 7       | 15.001                   | 15.006         | 425       | 60          |
| 8       | 15.005                   | 15.006         | 425       | 60          |

Table 2. The proximate analysis of the lignite and biomass samples (wt. % as used).

| Sample name | Moisture | Ash | Volatile matter | Fixed carbon* |
|-------------|----------|-----|-----------------|---------------|
| E. Lignite  | 14.7     | 34.6| 17.2            | 33.5          |
| Biomass    | 6.0      | 5.1 | 16.3            | 72.6          |

* By difference

Table 3. The ultimate analysis of Elbistan lignite and biomass samples (wt. % daf).

| Sample name | C      | H      | N      | S      | O*     |
|-------------|--------|--------|--------|--------|--------|
| E. Lignite  | 27.30  | 3.094  | 0.591  | 3.622  | 65.393 |
| Biomass     | 46.47  | 6.447  | 0.787  | 0.148  | 46.148 |

* By difference; daf: Dry ash free
3. Results and Discussions

Reaction time, temperature and pressure in the liquefaction are very important parameters. Therefore, in this study, the change of pressure and temperature with the reaction time was investigated. The results obtained are shown in Figure 2-9. As can be seen in Figure 2-5, the change of reaction temperature and pressure with time during the liquefaction of the apricot kernel shell were investigated at temperature of 325-400 °C. While there were significant changes in pressure during the first 30 minutes, no significant change in pressure was observed after 30 minutes. At the reaction temperature, while there were significant changes in the first 30 minutes, partial changes were observed after 30 minutes. By increasing of reaction temperature, these changes were more significant. As can be seen in Figure 6-9, the change of reaction temperature and pressure with time during the co-liquefaction of lignite and apricot kernel shell were investigated at temperature of 350-425 °C. While there were significant changes in temperature with reaction time, no significant change in pressure was observed.

Figure 1. Flow chart of classification of the liquefaction products [4]
Figure 2. The change of reaction temperature and pressure with time during the liquefaction of the apricot kernel shell (Temperature: 325 °C, particle size: 1.00 mm).

Figure 3. The change of reaction temperature and pressure with time during the liquefaction of the apricot kernel shell (Temperature: 350 °C, particle size: 1.00 mm).

Figure 4. The change of reaction temperature and pressure with time during the liquefaction of the apricot kernel shell (Temperature: 375 °C, particle size: 1.00 mm).
Figure 5. The change of reaction temperature and pressure with time during the liquefaction of the apricot kernel shell (Temperature: 400 °C, particle size: 1.00 mm).

Figure 6. The change of reaction temperature and pressure with time during the co-liquefaction of the lignite and apricot kernel shell (Temperature: 350 °C, particle size: 0.5 mm).

Figure 7. The change of reaction temperature and pressure with time during the co-liquefaction of the lignite and apricot kernel shell (Temperature: 375 °C, particle size: 0.5 mm).
Figure 8. The change of reaction temperature and pressure with time during the co-liquefaction of the lignite and apricot kernel shell (Temperature: 400 °C, particle size: 0.5 mm).

Figure 9. The change of reaction temperature and pressure with time during the co-liquefaction of the lignite and apricot kernel shell (Temperature: 425 °C, particle size: 0.5 mm).

Char yields and total conversions obtained in the co-liquefaction of the lignite and apricot kernel shell are given in Table 4 and 5. As can be seen from Table 4, with the increasing of reaction temperature, the total conversion is increased. The highest total conversion was obtained at 390 °C (93.10%). In the case of co-liquefaction of biomass and lignite, total conversions are decreased. While the highest total conversion obtained in biomass liquefaction is 93.10%, this ratio is 52.74% when biomass and lignite are co-liquefied.

Table 4. Char yields and total conversions obtained in the liquefaction of the apricot kernel shell.

| Exp. no | Sample amount (wt. as used) | Sample amount (daf*, g) | Char amount (daf*, g) | Char amount (daf, g) | Char yield (wt, %) | Total conversion (wt, %) |
|---------|-----------------------------|-------------------------|----------------------|----------------------|-------------------|------------------------|
| 1       | 30.0013                     | 26.668                  | 3.7994               | 3.488                | 13.08             | 86.92                  |
| 2       | 30.0003                     | 26.675                  | 3.6224               | 3.369                | 12.63             | 87.37                  |
| 3       | 30.0004                     | 26.67                  | 2.0237               | 1.854                | 6.95              | 93.05                  |
| 4       | 30.0001                     | 26.67                  | 2.0455               | 1.839                | 6.9              | 93.10                  |

* daf: Dry ash free; df: dry free
### Table 5. Char yields and total conversions obtained in the co-liquefaction of the lignite and apricot kernel shell.

| Exp. no | Sample amount (wt. as used) | Lignite/ biomass ratio | Sample amount (df*, g) | Char amount (df, g) | Char amount (daf*, %) | Char yield (wt, %) | Total conversion (wt, %) |
|---------|----------------------------|-----------------------|------------------------|---------------------|-----------------------|-------------------|------------------------|
| 5       | 30.0020                    | 1:1                   | 14.35                  | 11.6831             | 7.1175                | 49.60             | 50.40                  |
| 6       | 30.0100                    | 1:1                   | 14.35                  | 10.3498             | 7.8837                | 55.00             | 45.00                  |
| 7       | 30.0040                    | 1:1                   | 14.35                  | 9.645               | 6.7815                | 47.26             | 52.74                  |
| 8       | 30.0110                    | 1:1                   | 14.35                  | 9.100               | 6.9484                | 48.42             | 51.58                  |

As can be seen in the Figure 2 that there is no reaction occurs during the time after 30 min because of the constant pressure however from Figure 3 to 9 there are pressure increase that means more gaseous products occur. While looking time between temperature curves from Figure 3 to 9 give the favourable values. And it is obtained that at 400 °C temperature between time curve is the best reaction conditions with regard total conversion results of temperature 390 °C.

### 4. Conclusions

According to the pressure changes, it can be argued that the liquefaction reactions take place in the first 30 minutes effectively. Without using biomass, the total conversion was lower than only biomass liquefaction. If any catalyst was used total conversion would well improve on co-liquefaction. The study could be followed by using selective catalyst to make prediction about hydrogenation subjecting to temperature and pressure relations. The study shows that apricot kernel shell biomass is good for the liquefaction however Elbistan lignite combined with biomass liquefaction should be conducted by using a catalyst.

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