Hydrogen Transfer during Liquefaction of Elbistan Lignite to Biomass; Total Reaction Transformation Approach

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Abstract. Given the high cost of the tetraline solvent commonly used in liquefaction, the use of manure with EL is an important factor when considering the high cost of using tetraline as a hydrogen transfer source. In addition, due to the another cost factor which is the catalyst prices, red mud (commonly used, produced as a byproduct in the production of aluminium) is reduced cost in the work of liquefaction of coal, biomass, even coal combined biomass, corresponding that making the EL liquefaction an agenda for our country is another important factor. Conditions for liquefaction experiments conducted for hydrogen transfer from manure to coal; Catalyst concentration of 9%, liquid/solid ratio of 3/1, reaction time of 60 min, fertilizer/lignite ratio of 1/3, and the reaction temperature of 400 °C, the stirred speed of 400 rpm and the initial nitrogen pressure of 20 bar was fixed. In order to demonstrate the hydrogen, transfer from manure to coal, coal is used solely, by using tetraline (also known as a hydrogen carrier) and distilled water which is not hydrogen donor as a solvent in the co-liquefaction of experiments, and also the liquefaction conditions are carried out under an inert (N₂) gas atmosphere. According to the results of the obtained liquefaction test; using tetraline solvent the total liquid product conversion percentage of the oil + gas conversion was 38.3 %, however, the results of oil + gas conversion obtained using distilled water and EL combined with manure the total liquid product conversion percentage was 7.4 %. According to the results of cal orific value and elemental analysis, only the ratio of (H/C)atomic of coal obtained by using tetraline increased with the liquefaction of manure and distilled water. The reason of the increase in the amount of hydrogen due to hydrogen transfer from the manure on the solid surface of the coal, and also on the surface of the inner pore of the coal during the liquefaction, brings about the evaluation of the coal as a structure involved in the recycling through the liquefaction plant if it is being installed. As a result of this study, results obtained from oil + gas data shows that when distilled water is used instead of tetraline during liquefaction of EL combined with manure, abundant crude hydrogen transfer takes place not because of using distilled water as a solvent but only with manure considered as a hydrogen sources. Furthermore, while adding manure into coal of liquefaction is also an alternative for current oil production.

1. Introduction
Sufficient amounts of hydrogen must be present in the medium in order to convert the radicals formed during the liquefaction into small molecular weight stable compounds without joining them together and converting them into high molecular weight compounds [1]. Hydrogen transfer in the reaction medium takes place from the H₂ gas source (Figure 1), which is added to the spent coal waste, from the
solvent and from the outside [2]. Therefore, the hydrogen supply capacity of the solvent to be used for liquefaction must be very high [3]. Solvents such as creosote fat solubilizer, tetraline (C_{10}H_{12}), C_{10}H_{12}-alcohol mixture, C_{10}H_{12}-piren mixture, supercritical C_{10}H_{12}-Hexane (C_{6}H_{14}) mixture, H_{2}O and supercritical water are usually used as solvents in the liquefaction studies [4-6]. Solvent type used in liquefaction has a significant effect on both the cost of liquefaction and the efficiency of liquefaction [7, 8]. C_{10}H_{12} was used as the main solvent in this study. However, distilled water was used instead of C_{10}H_{12} as solvent to reduce the cost of liquefaction. Using distilled water for this study also shows how hydrogen transfer path from manure to coal fragment except of using tetraline as a most common hydrogen donor. To understand how amount of hydrogen transfer from manure to EL. Red mud, N
 atmosphere environment, and using without tetraline used, in order to calculate amount of hydrogen between before and after liquefaction experiments calculated.

Figure 1. Possible hydrogen radical transfer paths

2. Experimental
2.1. Materials
EL gathered from the field calls young lignite in Afsin-Elbistan thermal power plant, red mud was provided by the Eti-Aluminium Plant Research and Development department staff. Manure collected from Sultansuyu Agricultural Directorate of Malatya. Manure used as a biomass.

2.2. Procedure
In order to determine the most suitable solvent species, conversion of char, total conversion and liquefaction products was investigated using C_{10}H_{12} and distilled water as solvent. The liquid/solid ratio of 3/1, the mixing rate of 400 rpm, the catalyst type and concentration of 9% red mud and the initial N
 pressure of 20 bar, reaction time of 60 min and reaction temperature of 400 °C was fixed. The additional detailed experimental procedure is given in our previous article [9].

3. Results and discussions
3.1. Effect of solvent type
To calculate hydrogen quantity, the raw EL and manure samples conducted for their elemental analysis and the results are shown in Table 1. The char yield, total conversion and liquefaction product of each yields obtained at the end of the liquefaction process are summarized in Table 2 and shown in Figure 2. As can be seen from Figure 1, both the total conversion and the liquefaction product conversions obtained as a result of the liquefaction using C_{10}H_{12} as solvent were much higher than those obtained using the distilled water as solvent. When C_{10}H_{12} was used as the solvent, the total conversion was 72.5%, whereas when distilled water was used as the solvent, this ratio decreased to 31.6%. Similarly, PAS, AS and oil + gas conversions decreased from 21.0%, 13.2% and 38.3% to 19.8%, 4.4% and 7.4%, respectively. As can be seen from these results, when using distilled water as solvent, there is a
significant decrease in oil + gas and AS conversions, while there is a partial decrease in PAS conversion. Therefore, using distilled water as solvent in these conditions is not a suitable option. C_{10}H_{12} was chosen as the most suitable solvent species.

![Figure 2. Effect of solvent type (daf, %)](image)

**Table 1. Analysis of the lignite and waste samples**

|                        | Lignite | Manure |
|------------------------|---------|--------|
| **Proximate analysis (wt % as used)** |         |        |
| Moisture               | 32.2    | 8.1    |
| Ash                    | 23.5    | 22.3   |
| Volatile matter        | 21.8    | 57.0   |
| Fixed carbon\(^a\)     | 22.5    | 12.6   |
| **Ultimate analysis (wt % daf)** |         |        |
| C                      | 41.7    | 34.6   |
| H                      | 4.7     | 4.8    |
| N                      | 1.0     | 1.7    |
| S                      | 3.3     | 0.5    |
| O\(^a\)                | 49.3    | 58.4   |
| \((H/C)\text{atomic}\) | 1.4     | 1.7    |

\(^a\) by difference, daf: dry ash free
Table 2. The Experimental conditions and product yields of co-liquefaction

| Solvent type      | Conversion (%), daf |
|-------------------|---------------------|
|                   | Char Yield | Total | PAS | AS | Oil+gas |
| Tetraline         | 27.5       | 72.5  | 21.0 | 13.2 | 38.3    |
| Distilled water   | 68.4       | 31.6  | 19.8 | 4.4  | 7.4     |

*/ daf: dry ash free, PAS: Preasphaltene, AS: Asphaltene

3.2. Calculation of the oil+gas quantity

When tetraline is used as the solvent:

Coal amount (m_c): 40 g
Percentage of liquid product conversion obtained at the end of liquefaction (C): 72.5%
Amount of liquid product obtained at the end of liquefaction (m_l):

The input mass (daf) of 40 g of EL is calculated below;

\[ m_{l} = m_{c} \times C \]  
\[ m_{l} = 17.72 \times 0.725 = 12.847 \text{ g (daf)} \]  

The amount of oil + gas (m_{o+g}) is calculated as in equation (1).

Percent oil + gas conversion obtained at the end of liquefaction (C): 38.3%

\[ (m_{o+g}) = m_{l} \times C \]  
\[ (m_{o+g}) = 12,847 \times 0.383 \]  
\[ (m_{o+g}) = 4.9204 \text{ g} \]

When water is used as solvent;

Amount of coal (m_c) : 30 g
Amount of fertilizer (m_f) : 10 g
Total mass (m_t) : 40 g

The input mass (daf) of 30 g of EL and 10 g of Manure are calculated below;

\[ 30 \text{ g} \times (1-0.322-0.235) = 13.29 \text{ g (daf)} \]
\[ 10 \text{ g} \times (1-0.081-0.223) = 6.96 \text{ g (daf)} \]

Total input = 20.25 g (daf)
Percent liquid product conversion obtained at the end of liquefaction (C): 31.6%
Amount of liquid product obtained at the end of liquefaction (m_l):

\[ m_{l} = m_{c} \times C \]
\[ m_l = 20.15 \times 0.316 = 6.3674 \; g \; (daf) \]

The amount of oil + gas \((m_{o+g})\) is calculated as in equation (3).

Percent oil + gas conversion obtained at the end of liquefaction \((C)\) : 7.4%

\[ (m_{o+g}) = m_l \times C \]

\[ m_{o+g} = 0.4712 \; g \]

As can be seen after calculations, when tetraline was used as the solvent, for 40 g of EL liquefaction resulted 4.9204 g oil + gas (end product of hydrogenation) obtained, and for 10 g added with manure of the 30 g of Elbistan Lignite liquefaction with water as the solvent resulted 0.4712 g of oil + gas obtained. The results show us to consider if we use 121 ml tetraline, which decomposes with four atomic hydrogens to produce naphthalene effects, 10 times oil + gas production instead of using distilled water as a solvent. We can also calculate the oil + gas ratio per unit mass of Elbistan lignite to clearly see (wt/wt, %) of Oil + Gas.

For tetraline:

\[ \text{Oil+gas ratio} = \frac{4.9204 \; g}{17.72 \; g} = 0.2777 \; \text{g-oil+gas/ g-Input} \]

For water:

\[ \text{Oil+gas ratio} = \frac{0.4712 \; g}{20.25 \; g} = 0.0233 \; \text{g-oil+gas/ g-Input} \]

4. Conclusions

According to results, the topics should be presented results:

- When tetralin and distilled water were used as solvents, the oil + gas ratios obtained were 0.2777 g-oil+gas/g-Input and 0.0233 g-oil+gas/g-Input respectively. The using distilled water does not impact of hydrogen transfer and so oil+gas production. In addition, using only tetraline in liquefaction improves hydrogen transfer and so oil+gas production. So we can conclude that the source of hydrogen when using distilled water is manure.

- The factors of using Elbistan Lignite with manure, which both are also abundant reserves in our country, distilled water may be an inexpensive solvent, but since the effect on oil + gas yield is very low, the most suitable solvent has been proposed. Hence, by adding manure to coal due to the the surplus hydrogen excess should be presented as a new liquefaction plant proposal.

- Elbistan Lignite, which has abundant reserves in our country, offers both economical and sustainable solution. Red mud also used in this study with both experiments as a catalyst that reduces the cost of installation as well as decreases the cost of production of fuel-oil.

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