Co-Liquefaction of Elbistan Lignite with Manure Biomass; Part 1. Effect of Catalyst Concentration

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Abstract. The hydrogenation of coal by molecular hydrogen has not been appreciable unless a catalyst has been used, especially at temperatures below 500 °C. Conversion under these conditions is essentially the result of the pyrolysis of coal, although hydrogen increases the yield of conversion due to the stabilization of radicals and other reactive species. Curtis and his co-workers have shown that highly effective and accessible catalyst are required to achieve high levels of oil production from the coprocessing of coal and heavy residua. In their work, powdered hydrotreating catalyst at high loadings an oil-soluble metal salts of organic acids as catalyst precursors achieved the highest levels of activity for coal conversion and oil production. Red mud which is iron-based catalysed has been used in several co-processing studies. It was used as an inexpensive sulphur sink for the H2S evolved to convert Fe into pyrrohotite during coal liquefaction. In this study, Elbistan Lignite (EL) processed with manure using red mud as a catalyst with the range of concentration from 3% to 12%. The main point of using red mud catalyst is to enhance oil products yield of coal liquefaction, which deals with its catalytic activity. On the other hand, red mud acts on EL liquefaction with manure as a catalyst and represents an environmental option to produce lower sulphur content oil products as well.

1. Introduction

The catalyst type and concentration are crucial criteria in coal liquefaction research. In general, in liquefaction studies, NiMo, Al2O3, SO42−/ZrO2, ZnCl2, Fe2O3, Co2(CO)8, Mo(CO)6, Fe(CO)5, red mud, salt, oxide, and organometallic substances are frequently chosen to use as the catalyst [1-5]. Apparently, in this research, the red mud chosen to use as the catalyst was an industrial waste [6]. Actually, red mud, which in many cases is consisted of a mix of oxides of Fe, Ti, Al, and minimized quantities of Ca, Na, and Si, is a possible catalyst that can be chosen to use as an alternative at an industrial level. Moreover, red mud is still more cost-efficient than noble metals, along with potent metal oxides, after minor treatments. Incidentally, its chemical structure is described given up in Table 1. Additionally, the reaction phases of red mud throughout liquefaction are as follows [7]:

\[ 3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \] (1)
Fe₃O₄ + H₂ → 3FeO + H₂O \hspace{1cm} (2)

FeO + H₂ → Fe + H₂O \hspace{1cm} (3)

Overall reaction; 3Fe₂O₃ + 9H₂ → 6Fe + 9H₂O \hspace{1cm} (4)

The outcomes support the view that a variety of metal oxide catalysts such as red mud are resistant to catalyst toxic substances such as sulphur and can maintaining their catalytic activity. Nevertheless, the effectiveness of catalysts like these has actually been low, primarily due to their minimized area and the dispersion level of catalytic particles in an offered system of reacting volume. Quite the opposite on the contrary, treatments such as sulfidation and size decrease can enhance the activity of such alternative catalysts. Furthermore, they are chosen to be used just once, and there is no requirement to recuperate them, unlike high-cost catalysts that need to be recuperated, [7].

| Compounds | %        |
|-----------|----------|
| SiO₂      | 15.74    |
| Al₂O₃     | 20.39    |
| Fe₂O₃     | 36.94    |
| TiO₂      | 4.98     |
| CaO       | 2.23     |
| MgO       | -        |
| K₂O       | -        |
| Na₂O      | 10.10    |
| L.O.I.    | 8.19     |
| V₂O₅      | 0.05     |

2. Experimental
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. Beef, horse and chicken manure collected from Sultansuyu Agricultural Directorate of Malatya. Waste plastic collected from plastic water bottle in Inonu University campus. Tea pulp collected from some private coffeehouse in Malatya city, Turkey. In this study, red mud was used as catalyst and the concentration was changed between 3-12%. Reaction temperature 400°C, reaction time 60 min, liquid/solid ratio 3 and waste/lignite ratio 1/3 was fixed. Manure was used as biomass. The experimental procedure is given in our previous article [8].

3. Results and discussions
3.1. Effect of catalyst concentration
Red mud, which is iron-based catalysed has been used in several co-processing studies [9]. It was used as an inexpensive sulphur sink for the H₂S evolved to convert Fe into pyrohotite during coal liquefaction [9, 10]. The main point of using red mud catalyst is to enhance OG yield of coal liquefaction [11], which deals with its catalytic activity [12]. On the other hand, in this study, red mud acts on EL liquefaction with manure as a catalyst and represents an environmental option to produce lower sulphur content OG’s as well. With reference to figure out the most suitable catalyst concentration for the liquefaction experiments, a 3:1 solvent to solid ratio, a stirring speed of 400 cycles/min, a temperature level of 400°C, a time period of 60 minutes, and a preliminary N₂ pressure of 20 bar was conducted. In addition, manure
was used as a waste type. As can be revealed in Table 2, the effect of catalyst load on the yield and product distributions arising from co-processing. Furthermore, as displayed in Table 2, a boost in the catalyst concentration between 3\% - 9\% led to OG yields enhancing considerably by 8.2\% while total conversion did not alter significantly. To some extent, the boost in OG yields with the increase in catalyst concentration is because of cracking of liquid products (PAS and AS) to OG. Additionally, as can be seen in Table 2 and detailed in Figure 1, when enhancing the catalyst concentration from 9\% to 12\%, OG yields reduced from 38.3\% to 28.3\%. No doubt, the reduction in OG yields through an increase in catalyst concentration results from the cracking of liquid products to gas leading to a boost in char yield [10]. For that reason, by thinking about the yield values acquired, the optimum catalyst concentration was discovered to be 9\% and red mud revealed a catalytic potency when the outcomes were compared to the experiment performed in the absence of a catalyst. When it comes to existence catalysis (Fe_2O_3 based as red mud), OG yields of the liquefaction products from coal under H_2 environment as well as oil yields from biomass enhances [9, 11, 12]. Using manure combined with EL produced the higher sulphur content of char than using EL alone (by the same red mud concentration, 9\%). That means, adding manure, increased the catalytic effect of red mud for reducing more sulphur as a pyrrhotite form on chars [8]. It represents that EL liquefaction with manure catalysed by 9\% red mud is more environmental method than burning of EL. As a consequence, red mud (an industrial waste) was recommended as a catalyst for the EL coliquefaction procedure due to its financial and environmental benefits.

Table 2. The experimental conditions and product yields of co-liquefaction

| Exp. No | Waste type | Catalyst concentration (wt. %) | Liquid sol. | Waste t lignite solid (min) | T (°C) | Char Yield (daf, \%) | Total Conver. Yield | PAS Yield | AS Yield | Oil+gas Yield |
|---------|------------|--------------------------------|-------------|-----------------------------|-------|----------------------|---------------------|-----------|-----------|---------------|
| 1       | Manure     | 3                              | 1/3         | 60                          | 400   | 24.8                 | 75.2                | 29.0      | 16.1      | 30.1          |
| 2       | Manure     | 3                              | 1/3         | 60                          | 400   | 25.3                 | 74.7                | 24.9      | 15.4      | 34.4          |
| 3       | Manure     | 6                              | 1/3         | 60                          | 400   | 25.2                 | 74.8                | 25.9      | 15.2      | 33.7          |
| 4       | Manure     | 9                              | 1/3         | 60                          | 400   | 27.5                 | 72.5                | 21.0      | 13.2      | 38.3          |
| 5       | Manure     | 12                             | 1/3         | 60                          | 400   | 26.6                 | 73.4                | 29.0      | 16.1      | 28.3          |

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

Figure 1. Effect of catalyst concentration.
4. Conclusions

Using red mud in co-liquefaction process increased OG yields as well as showed the optimum catalytic activity with 9 % concentration to decrease the economic cost. Making use of biomass as a hydrogen donor assists the more hydrogen transfer to coal connected with C_{10}H_{12} as well as red mud. Subsequently, using biomass and red mud minimized the cost of direct coal liquefaction procedure too. On top of that, these outcomes open the new possibility of developing direct coal liquefaction plants. The high catalyst concentration is a parameter that adversely affects the reactor feed rate. In our study of catalytic increase, it was observed that there was no significant increase in total conversion at values increasing from 3% to 9%. In the case where the catalyst concentration increased by 3% to 9%, the PAS yield decreased from 24.9% to 21%. AS yield decreased by 15.4% to 13.2% while oil + gas yield increased from 34.4% to 38.3%.

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