Co-Liquefaction of Elbistan Lignite with Manure Biomass; Part 3 - Effect of Reaction Time and Temperature

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Abstract. Most of the liquefaction process were carried out in a batch reactor, in which the residence time of the liquefaction products is long enough to favour the retrogressive reactions. To minimize retrogressive reactions, the liquefaction of coal was carried out in a flowing solvent reactor in which a fixed bed of coal is continuously permeated by hot solvent. Solvent flowing through the coal bed carries the liquefaction products out of the reactor. Unlike experiments carried out under similar conditions in a batch reactor no increase in solid residue is observed during long time high temperature runs in the flowing solvent reactor. There is a greater appreciation of the importance of retrograde, or polymerization, reactions. If the free radicals formed when coal breaks down are not quickly capped with hydrogen, they react with each other to form large molecules that are much harder to break down than the original coal. Reaction time impacts both the co-liquefaction cost and the product yield. So as to study this idea, the experiments of Elbistan Lignite (EL) with manure co-liquefaction carried out by changing the reaction time from 30 to 120 minutes. As a result, the greatest oil products yields obtained at 60 minutes. Therefore, by thinking about the oil products yield values acquired, the optimal reaction time was obtained to be 60 minutes for Elbistan lignite (EL) with manure liquefied with the temperature of 350°C and 400°C. Above 425°C did not examine because solvent (tetraline) loses its function after 425 ºC. The obtained optimum temperature found 400°C due to higher total conversion of liquefaction products and also oil+gas yields.

1. Introduction

The free radicals produced by the coal liquefaction process react with the H· released by H_2 or a donor solvent such as tetraline ($C_{10}H_{12}$), N-methyl-2-pyrrolidinone (NMP) and toluene (C_7H_8) throughout the hydrogenation process [1, 2]. Direct hydrogen injection is expensive, and strict conditions in the reactor need to be observed. For that reason, a hydrogen provider (such as biomass with coal) might fix these problems. Coal and biomass dissolution (co-liquefaction) enables a hydrogen transfer from biomass to coal in order to enhance oil yields. Hydrogen comes primarily from the destruction of cellulose, hemicellulose, or perhaps lignin. Soybean straw offers hydrogen for the hydrogenation of the C=C bonds of sunflower oil during the co- deoxy-liquefaction process [3]. The overall conversion of binary co-liquefaction reaction can be enhanced when single reactions are compared to component reactions [4]. This is due to the fact that co-liquefaction has the ability to synergize the production of light-weight, value-added products from biomass and coal [5, 6]. As an outcome, we can observe the existence of electrophilic reactions on both sides of the reaction [7, 8]. the transfer of hydrogen from $C_{10}H_{12}$ is the

most trustworthy and widely known procedure for enhancing the rate of coal conversion [9], for that reason, liquefaction research is carried out choosing to use N_2 gas rather of H_2 gas in accordance with previous coal liquefaction research studies choosing to use N_2 gas [6-8, 10-12]. Comparing to early studies, in this study, to find hydrogen transfer from manure to coal N_2 gas uses instead of H_2 gas. Observations for the co-liquefaction experiments indicate that EL combined with the manure, manure offers as a hydrogen donor. The demonstrated co-liquefaction system opens a door to the further development of other biomasses to use as a hydrogen donor.

2. Experimental
2.1. Materials
EL gathered from the field calls young lignite in Afsin-Elbistan thermal power plant, Red mud was sent by the Eti-Aluminium Plant Research and Development department staff. Beef, horse and chicken manure collected from Sultansuyu Agricultural Directorate of Malatya. In this study, red mud was used as catalyst and the concentration of 9 %. Reaction temperature changed with 350°C and 400°C, reaction time from 30 to 120 min., in addition liquid/solid ratio 3 and waste/lignite ratio 1/3 was fixed constant. The experimental procedure is given in our previous article [13].

3. Results and Discussions
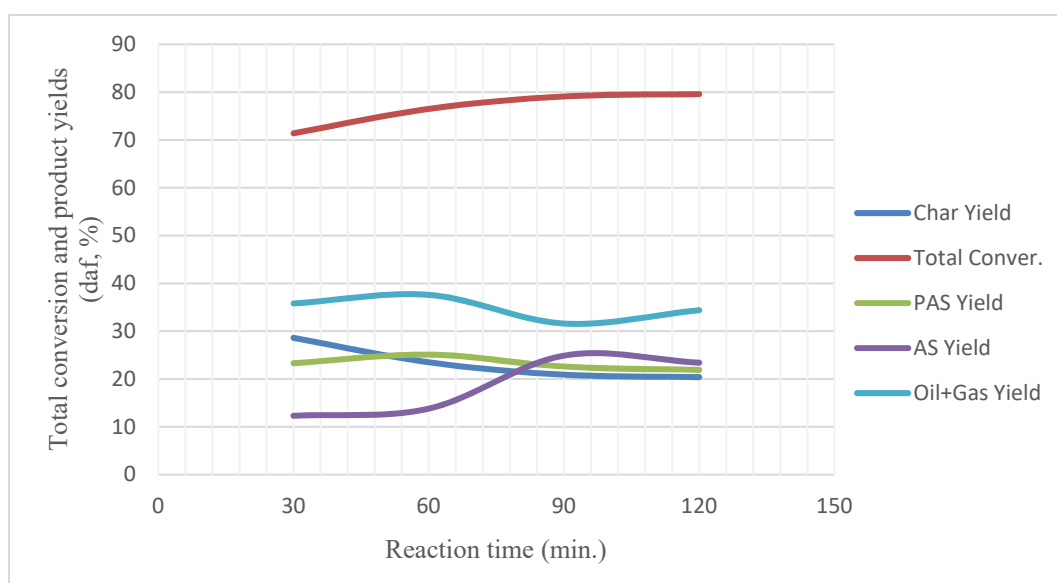### 3.1. Effect of reaction time
Reaction time impacts both the co-liquefaction cost and the product yield. So as to study this idea, the experiments were carried out by changing the reaction time from 30 to 120 minutes. In short, as shown in Table 1, the increase in reaction time from 30 to 120 minutes resulted in an increase in overall yield from 71.4% to 79.6%; OG and PAS yields were not considerably changed, and AS yield increased from 12.3% to 23.4% respectively. Thus, the increase in the reaction time from 30 to 90 minutes resulted in an increase in both total conversions and AS yields. Nevertheless, PAS yield was not altered and OG yields reduced. Furthermore, AS yield considerably enhanced, and there was a partial increase in the total conversion rate when the reaction time was extended from 60 to 90 minutes. However, when changing the time of reaction beyond 90 minutes, both total conversion and liquid products from liquefaction were the same. As a result, the greatest OG yields were gotten at 60 minutes. Therefore, by thinking about the yield values acquired, the optimal reaction time was discovered to be 60 minutes.

Table 1. The Co-liquefaction experiments and results

Exp. No	Waste type	Catalyst cont.	Liquid solid (%, wt)	Waste lignite	t (min)	T (°C)	Char Yield	Total Conver.	PAS Yield	AS Yield	Oil+gas Yield
Reaction time											
1	Manure	9	3	1/1	30	400	28.6	71.4	23.3	12.3	35.8
2	Manure	9	3	1/1	60	400	23.5	76.5	25.1	13.8	37.6
3	Manure	9	3	1/1	90	400	20.9	79.1	22.6	24.9	31.6
4	Manure	9	3	1/1	120	400	20.4	79.6	21.9	23.4	34.3
Reaction temperature											
5	Manure	9	3	1/1	60	350	39.4	60.6	20.2	10.5	29.9
2	Manure	9	3	1/1	60	400	23.5	76.5	25.1	13.8	37.6

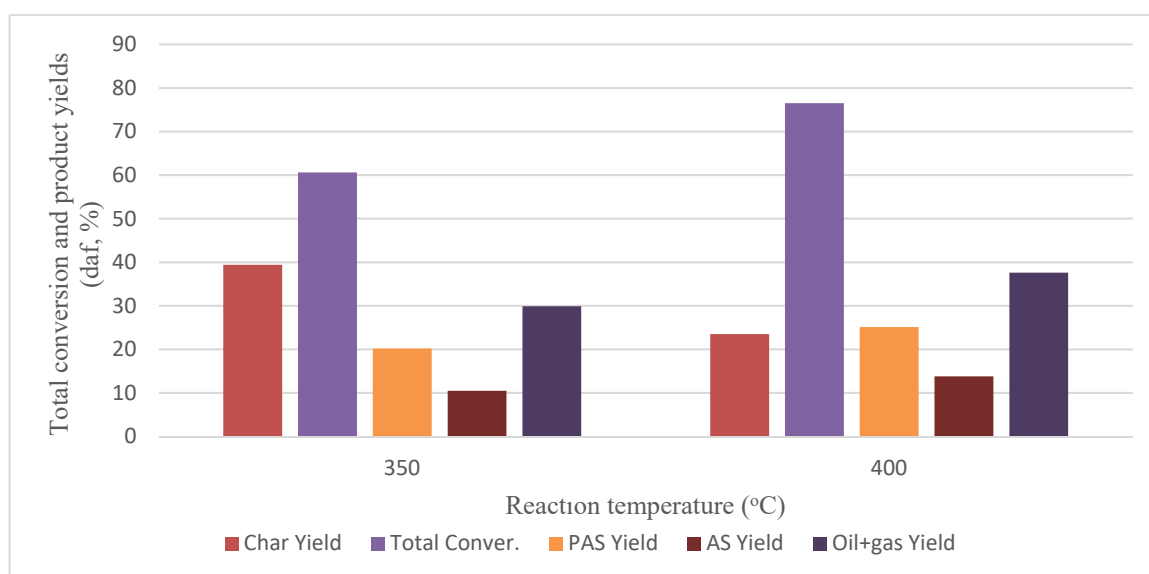*/ PAS: Preasphaltene, AS: Asphaltene, daf: dry ash free.

Even though, at high-temperature levels of liquefaction and with longer reaction times the combined result reduces due to the increase in the liquefaction result of the coal and the failure of the system to contribute hydrogen under these settings, consequently resulting in the increase in the speed of regressive condensed reactions. In general, the result enables greater oil production and significantly reduces the total conversion due to liquid to gas products and char formation through condensing, re-polymerising, and cyclizing the liquid products [2, 14, 15].

Figure 1. Effect of reaction time

3.2. Effect of reaction temperature

As a matter of fact, reaction temperature has the same significance as the reaction time on the coal liquefaction [16, 17]. To show its impact, the temperatures of reactions were raised between 350°C and 400°C. Although, $C_{10}H_{12}$ breaks down above 425°C. Hence, as revealed in Tables 1, when raising the temperature of the reaction from 350°C to 400°C, both total conversions and OG yields increased considerably.

Figure 2. Effect of reaction temperature

In the same way, when increasing the reaction time, both lignite and waste decayed rapidly, so the total conversion that considerably increased.

Furthermore, at higher reaction temperatures, PAS and AS decompose into lighter molecules – such as oils and gasses – effectively so OG yield considerably increased, while PAS and AS yield reduced. Therefore, by considering the yield values obtained, the optimum reaction temperature was found to be 400°C. Overall, the results showed that both total conversion and the yields of products increased with the increase in temperature [17].

4. Conclusions

Due to the increase in reaction durations, partial changes were observed in the total conversion, OG, and PAS yields while the AS yield increased. The most suitable reaction time was picked to 60 minutes for increasing the extreme formation from the coal and waste product and to effectively saturate the formed radicals with hydrogen.

As a result of the liquefaction of EL and manure, the total conversion got at 400°C reaction temperature is higher compared with the PAS and AS yields at 350 °C. In addition, there is a partial decline in OG yield. Nevertheless, in order to break down lignite effectively and convert it to radicals, the reaction temperature should be set at a minimum of 375°C; for this factor, the temperature was selected as 400°C.

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