

## Co-liquefaction of Elbistan Lignite with Manure Biomass; Part 2 - Effect of Biomass Type, Waste to Lignite Ratio and Solid to Liquid Ratio

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**Abstract.** Most coal hydrogenation processes require a large quantity of hydrogen. In general, a coal derived liquid such as anthracene oil was used as a hydrogen donor solvent. Tetralin, partially hydrogenated pyrene, phenanthrene and coal-derived solvents, which contain hydroaromatic compounds, are efficient solvents to donate hydrogen. In an attempt to reduce the high cost of hydrogen, part of the hydrogen was replaced by a low cost hydrogen donor solvent. This must be hydrogenated during or before the process and recycled. To reduce the cost of hydrogen donor vehicles instead of liquids recycled from the liquefaction process or several biomass types, industrial by products, liquid fractions derived from oil sands bitumen were successfully used to solubilize a coal from the past. In an attempt to reduce the high cost of hydrogen, part of the hydrogen was replaced by a low cost hydrogen donor solvent. However, when hydrogen is supplied from the hydroaromatic structures present in the solvent, the activity of coal minerals is too low to rehydrogenate the solvent in-situ. Nevertheless, a decrease of using oxygen, in addition to enhanced usage of the hydrogen supply by using various waste materials might lead to a decrease of the cost of the liquefaction procedure. So instead of using tetralin another feeding material such as biomass is becoming another solution improving hydrogen donor substances. 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, early studies which are related to liquefaction of coal with biomass generally focus on the synergetic effects of coal while biomass added. Early studies which are related to liquefaction of coal with biomass generally focus on the synergetic effects of coal while biomass added. Alternatively, to understand the hydrogen transfer from biomass to coal, in this study, Elbistan Lignite (EL) with manure, tea pulp and waste plastic liquefied and to understand hydrogen quantity change after liquefaction,  $(H/C)_{\text{atomic}}$  ratio of products obtained. Due to the highest oil conversion of manure biomass and highest  $(H/C)_{\text{atomic}}$  ratio results show manure is the favourable biomass for EL amongst the other biomass used. And liquid/solid ratio optimized. About high total conversion of oil products the optimum ratio obtained as 3/1. And also EL with manure liquefied with the w/EL ratio between 0:1 to 1:1. As a result, by thinking about the yield values obtained, the optimum waste to lignite ratio found to be 1:1.



## 1. Introduction

There has been a quick boost in worldwide energy production during this century, and today non-renewable fuel sources such as coal, petroleum, and natural gas are used to meet 80% of the world's energy requirement [1-4]. Direct hydrogen injection is expensive, and strict conditions in the reactor need to be observed. In other words, during co-liquefaction, biomass might be thought about as a hydrogen donor, as an assistant to the liquefaction process and as a minimized danger to the environment [5-8]. The technology for co-liquefaction has currently been established. And is in use by pilot-plants [9]. For example, Headwaters Inc. and Axens have gone into a collaboration to establish direct coal liquefaction technology for the production of clean fuel by choosing to use biomass and wastes (co-liquefaction) [10, 11].

As an outcome, we can observe the existence of electrophilic reactions on both sides of the reaction [12, 13]. In this case, the separate liquefaction of wastes is not a favored procedure, and the liquefaction trials were performed both with single lignite and lignite combined with waste items. As for, we studied an effort at the co-liquefaction of EL with shredded plastic bottles (Polytetrafluoroethylene, PTFE), beef and cattle manure, and a prepared tea waste product called tea pulp. In addition, the coliquefaction of the EL and waste materials was carried out in both non-catalytic conditions and catalytic conditions in the existence of nitrogen gas ( $N_2$ ) and the impacts of process parameters such as waste type, catalyst concentration, liquid to solid ratio, waste to lignite ratio, reaction time, and temperature level on the liquefaction yield were examined.  $N_2$  gas was chosen to use rather of reactive  $H_2$  gas.  $H_2$  gas influences the liquefaction performance in a favourable method, although it enhances liquefaction expenses.

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

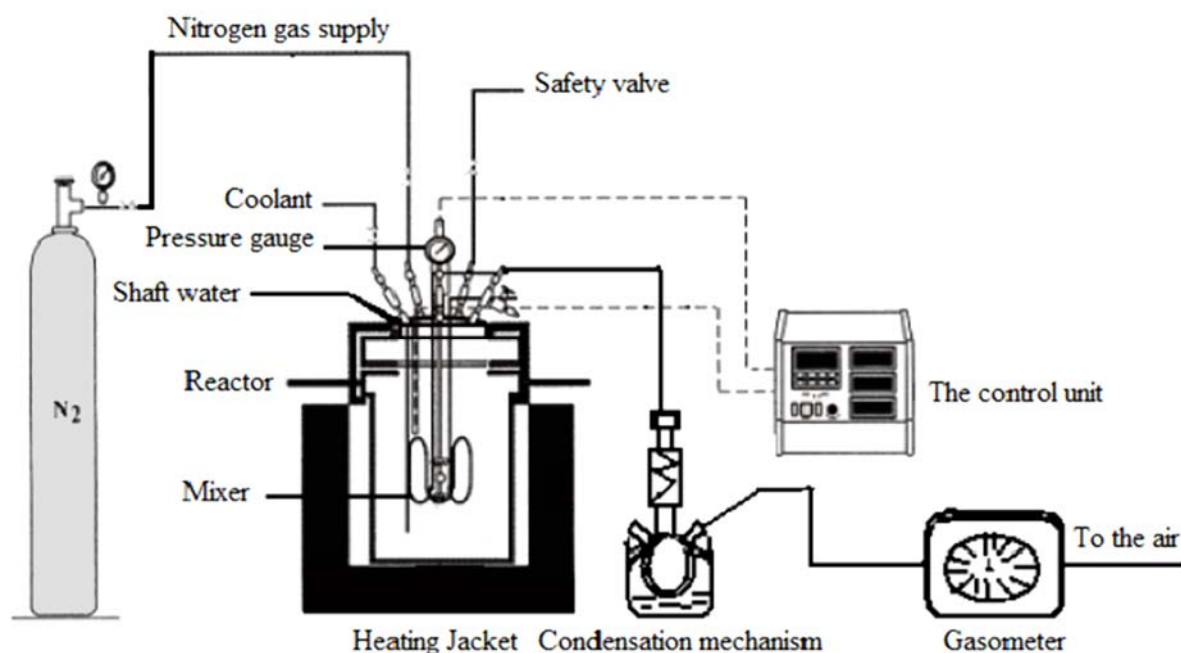
EL gathered from the field calls young lignite in Afsin-Elbistan thermal power plant, red mud was provided by the Eti-Aluminium Plant Research and Development department staff. Manure collected from Sultansuyu Agricultural Directorate of Malatya. Waste plastic collected from plastic water bottle in Inonu University campus. Tea pulp collected from some private coffeehouse in Malatya city, Turkey.

### 2.2. Liquefaction procedure

EL with a particle size of less than 1.5 mm was selected to use in this research study. To begin with, it was air-dried at room temperature level for 24 h prior to use. In the second stage, red mud (by product of the Bayer process), manure (horse manure/beef manure/chicken manure 1:1:1 weight blended) waste plastic (PTFE), and tea pulp (domestic waste) with a particle size of less than 1 mm, were chosen to use in this study. Similarly, they were air-dried at room temperature level for 24 h prior to use. Finally, the beef and chicken manure were air-dried prior to blending.

Liquefaction experiments during the course of a day (6-9 hours) were carried out both with lignite combined with the waste materials and lignite alone. After liquefaction, the soluble products were divided into solubility groups, i.e., preasphaltenes and asphaltenes ( $C_7H_8$  solubles) and oils (n-hexane,  $C_6H_{14}$  solubles), through continuous extraction with  $C_7H_8$  (Riedel de Haen, 99.7% purity) then  $C_6H_{14}$  (Riedel de Haen, 95% purity).

As displayed in Figure 1, the experimental system includes of a  $N_2$  gas tube (Habas, 99.999% purity), autoclave, condenser, and temperature level control system, and gas meter. Figure 2 reveals a schematic of the procedure for the liquefaction experiments.



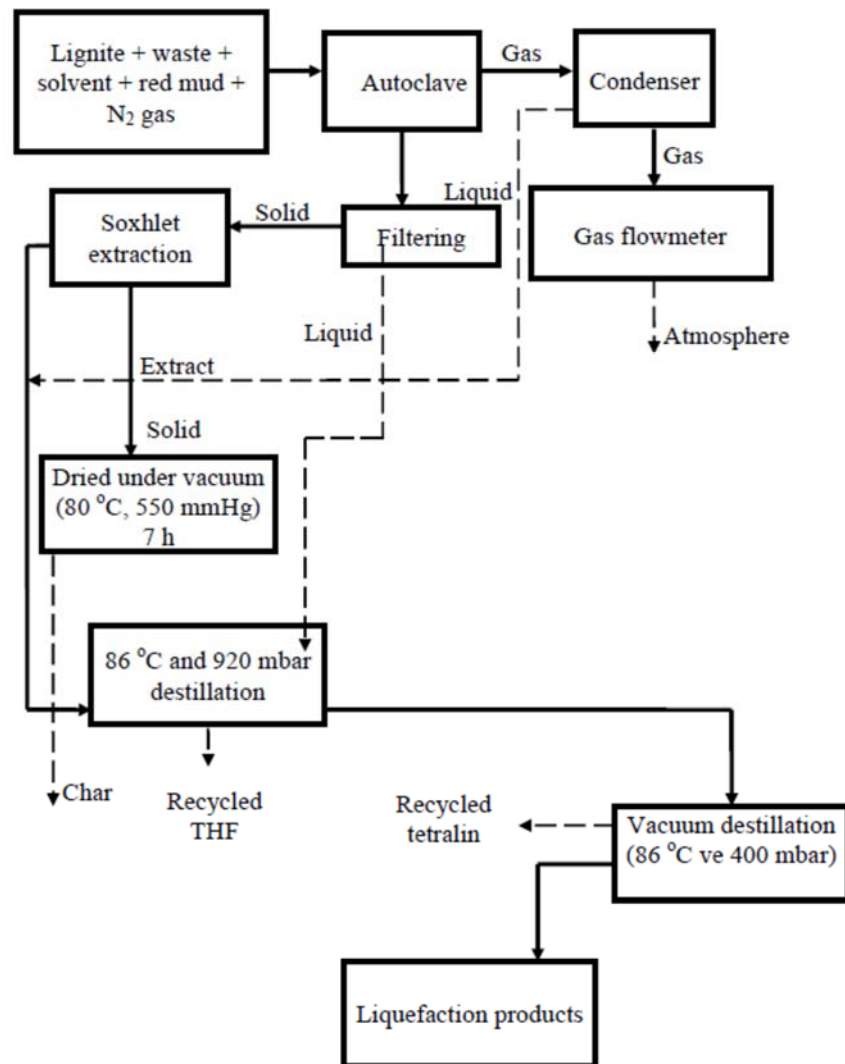
**Figure 1.** The experimental setup

To start with, in an experiment performed to analyze liquefaction effectiveness in the catalytic conditions, 30 g of lignite, 10 g of waste (waste to lignite ratio, 1:3), 1.20 g of red mud, and 121 ml of solvent (C<sub>10</sub>H<sub>12</sub>, Merck, 98% purity) were put into the autoclave. In order to eliminate the air in the reaction system, the autoclave was cleaned up with N<sub>2</sub> gas for 10 minutes by opening the input and output valves. Furthermore, the gas outlet valves were then closed and the N<sub>2</sub> gas was fed to the reaction medium up until the preliminary pressure reached 20 bar. To examine whether there was any leak from the autoclave, it was inspected for any reduction in pressure after 10 minutes.

After the system prep works, the autoclave was heated up at a speed of 3-4°C/minute by triggering the heating system (ceramic fibre) and stirrer, up until it reached the picked expected reaction temperature level. Secondly, A reaction time period with 60 minute was enabled at the chosen reaction temperature level with 400 °C, and throughout both heating and reaction was occurring, a consistent stirring speed of 400 rpm (cycles/min) speed was preserved. Both the mixer and heating unit were switched off in series at the end of the reaction stage, and around 60 minutes were provided to enable the collapse of any small little particles suspended in the gas of the reaction medium. In the third stage, by opening the gas discharge valve of the autoclave and by passing the gas products through a cooler, the condensable products wandering with the gases were captured (Figure 2).

After determining the overall volume of non-condensable gasses (roughly, 10-21 L), they were launched into the atmosphere. After the gas-discharge procedure was finished, the autoclave was cooled around 1-2 h in order to reach the ambient temperature level (Figure 2).

In the next step, the solid and liquid products were put into a beaker. In order to clean up the particles and liquid products sticking to the walls of the autoclave and the stirrer, they were cleaned with 200 ml of (CH<sub>2</sub>)<sub>4</sub>O (Carlo Erba, 99.5 % purity). Finally, the autoclave was then dried in prep work for the next test.



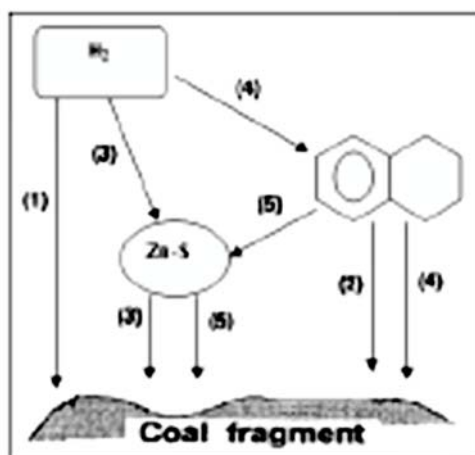
**Figure 2.** Flow chart of the experimental

### 3. Results and Discussions

#### 3.1. Effect of waste type

Early studies which are related to liquefaction of coal with biomass generally focus on the synergetic effects of coal while biomass added [14, 15]. Alternatively, to understand the hydrogen transfer from biomass to coal, in this study, the  $(H/C)_{\text{atomic}}$  ratio (Table 1) and the total conversion deal with OG yields (Table 2) were determined. The obtained total conversion and liquefaction production yield, as an outcome of the co-liquefaction process, are displayed in Table 2. Due to the co-liquefaction of EL by manure, tea pulp, and waste plastic under catalytic conditions, the greatest total change was acquired by utilizing manure and tea pulp. As can be seen in Table 2, the highest OG yield was obtained by using manure. Among the most vital coal liquefaction criteria is an  $(H/C)_{\text{atomic}}$  ratio. As apparent from Table 1, manure had the greatest  $(H/C)_{\text{atomic}}$  ratio of all the wastes that were used. In this case, the hydrogen donor solvent needs the addition of waste, there need to be a choice for those which have high  $(H/C)_{\text{atomic}}$  ratio instead of those which have a greater lignite ratio [12]. In such a circumstance, the hydrogen transfer from manure to coal (e.g., using 5th path (Figure 3) [13]) assists in the co-liquefaction procedure.

The Table 1 also shows the data if red mud concentration increased the  $(H/C)_{\text{atomic}}$  ratio not significantly changed. In this case, hydrogen transfer should be manure to coal fragment using 4th path in Figure 3



**Figure 3.** Possible hydrogen radical transfer paths

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

	Lignite	Manure	Tea pulp	Waste plastic	Char 1	Char 2	Char 3
<i>Proximate analysis</i> (wt % as used)							
Moisture	32.2	8.1	11.1	0.4	-	-	-
Ash	23.5	22.3	3.1	0.1	-	-	-
Volatile matter	21.8	57.0	68.9	87.7	-	-	-
Fixed carbon <sup>a</sup>	22.5	12.6	16.9	11.8	-	-	-
<i>Ultimate analysis</i> (wt % daf)							
C	41.7	34.6	46.9	61.5	19.0	17.4	14.6
H	4.7	4.8	6.4	4.2	1.5	1.3	1.0
N	1.0	1.7	3.4	-	0.7	0.4	0.2
S	3.3	0.5	0.5	0.1	1.6	1.7	1.7
O <sup>a</sup>	49.3	58.4	42.8	34.2	77.2	79.2	82.5
$(H/C)_{\text{atomic}}$	1.4	1.7	1.6	0.8	0.95	0.90	0.82

Char 1: Char after alone EL liquefaction + Red mud (9%)

Char 2: Char after EL with manure liquefaction + Red mud (3%)

Char 3: Char after EL with manure liquefaction + Red mud (9%)

<sup>a</sup> : by difference

daf: dry ash free

From this, it is clear that the change derived by co-liquefaction of EL with manure, tea pulp and as well as alone lignite is higher than that originated from the co-liquefaction with waste plastic. As a result, the greatest OG yield was gotten by using manure. For that reason, it is possible to assert that EL co-liquefaction with manure seems a much better technique in regards to raising the total conversion change along with an OG yield change. As a consequence, waste plastic and tea pulp are not as appropriate for the co-liquefaction process as manure due to its total conversion. For that reason, Biomass selection is essential for such co-liquefaction conditions. Furthermore, it can be concluded that existence of manure enhances the action [16] in the development of oil, provides increase to much greater figures for H/C and enables a lower oxygen content in liquid products [17] than liquefaction of coal alone [3]. As can be seen in Table 1, after liquefaction of EL with the manure char's (H/C)<sub>atomic</sub> ratio is lower than only liquefaction of EL char's (H/C)<sub>atomic</sub> ratio in regard to soluble products H atomic value enhanced.

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

Exp. No	Waste type	Catalyst cont. (wt.%)	Liquid Solid	Waste Lignite	t (min)	T (°C)	(%, daf)			
							Total Conv.	PAS Yield	AS Yield	Oil+gas Yield
Waste type										
1	Manure	3	3	1/3	60	400	74.7	24.9	15.4	34.4
2	Tea pulp	3	3	1/3	60	400	59.6	26.8	11.1	21.7
3	Waste plastic	3	3	1/3	60	400	74.7	28.4	18.0	28.3
Liquid/solid ratio										
4	Manure	9	1	1/3	60	400	70.4	30.5	24.4	15.5
5	Manure	9	3	1/3	60	400	72.5	21.0	13.2	38.3
6	Manure	9	6	1/3	60	400	72.0	26.0	22.9	23.1
7	Manure	9	9	1/3	60	400	74.8	27.1	22.2	25.5
Waste/lignite ratio										
8*	-	9	3	-	60	400	63.1	44.0	12.9	6.20
9	Manure	9	3	1/1	60	400	76.5	25.1	13.8	37.6
10	Manure	9	3	1/2	60	400	75.5	32.0	14.9	28.6
5	Manure	9	3	1/3	60	400	72.5	21.0	13.2	38.3
11	Manure	9	3	1/4	60	400	72.1	34.3	11.4	26.4
12	Manure	9	3	1/6	60	400	69.6	36.7	12.5	20.4

\*Experiment 8 is the liquefaction of lignite alone, PAS: Preasphaltene, AS: Asphaltene, daf: dry ash free.

The formulation of calculating total conversion and the products yield shown below:

Char yield :

$$\text{Char (daf, \%)} = \text{char (g, daf) / sample (g, daf)} \times 100 \quad (1)$$

$$\text{Total conversion (daf, \%)} = 100 - \text{char (daf, \%)} \quad (2)$$



Yield of the liquefaction products:

$$\text{PAS\%} = \text{PAS (g)}/\text{sample (daf, g)} \times 100 \quad (3)$$

$$\text{AS\%} = \text{AS (g)}/\text{sample (daf, g)} \times 100 \quad (4)$$

$$\text{OG\%} = \text{Total conversion (daf, \%)} - \text{PAS\%} - \text{AS\%}. \quad (5)$$

### 3.2. Effect of liquid to solid ratio

Apart from catalyst, another crucial function in the coal liquefaction procedures is played by the solvent [1, 2, 4, 18]. Whereas, there are two functions that are essential for a solvent to be reliable; namely, it need to be a deserving physical solvent for coal products, and it must have an H shuttling or H-donor capacity for it to hydrogenate and support any complimentary radicals launched by the coal [19]. Furthermore, some kinds of solvent, in certain, have comparable results as the catalyst [20]. For example,  $\text{C}_{10}\text{H}_{12}$  is a high-cost solvent and its extremely aromatic compounds were observed in the oil produced [18]. Nevertheless, if it can be recycled and reused, lower operational expenses and greater oil content can be offered [21]. In addition, the liquefaction products might likewise be used as a donor solvent in location of  $\text{C}_{10}\text{H}_{12}$ . In this study, hydrogen-donating tetralin ( $\text{C}_{10}\text{H}_{12}$ ) was used as the solvent, and the experiments were carried out by altering the liquid-to-solid ( $\text{C}_{10}\text{H}_{12}$ :(lignite+waste)) ratio between 1:1 and 9:1. Additionally, by enhancing the liquid to solid ratio from 1:1 to 3:1, the total conversion and liquefaction output yield increased. Moreover, a considerable increase in the OG yields was observed at a liquid to solid ratio of 3:1 by 22.8%, and the OG yields reduced in percentage to the enhancing solvent- to-solid ratio (see Table 2). Similarly, increasing the liquid to solid ratio from 3:1 to 6:1, the OG yields reduced from 38.3% to 23.1%, the PAS yield increased from 21.0% to 26.0%, and the AS yield enhanced from 13.2% to 22.9% (see Table 2). As a consequence of that reason, by thinking about the yield values acquired, the optimum liquid to solid ratio was identified to be 3:1. This reveals that soluble yields of  $(\text{CH}_2)_4\text{O}$  do not increase with the liquid-to-solid ratio from a lower to a higher value, but are restricted by the existence of solid which consists of a higher amount of residue or char in order to ensure the chemical stability of the free radicals [3, 22].

### 3.3. Effect of waste to lignite ratio

Partially due to the expense of hydrogen, the production of liquids from coal is less competitive financially in contrast with the expense of the technology used in petroleum. Nevertheless, a decrease of using oxygen, in addition to enhanced usage of the hydrogen supply by using various waste materials might lead to a decrease of the cost of the liquefaction procedure [23, 24]. In this study, hydrogen donor biomass manure, waste plastic, and tea pulp were used and the experiments were performed by altering the waste to lignite ratio between 0:1 to 1:1. As displayed in Table 2, by changing the waste to lignite ratio from 0:1 to 1:1, the total conversion was slowly enhanced by 13.4% while OG yields considerably increased by 31.4%, PAS yield substantially reduced by 18.9% and AS yield just partly altered.

Therefore, this might be of significance for the reactions of biomass conversion to fuel ingredients as they require hydrogen to reduce oxygen content. Moreover, the optimal total conversion was 76.5%, and was attained from a 1:1 waste to lignite ratio, the optimum OG yields were 38.3% and was accomplished from a 1:3 waste to lignite ratio. As a result, by thinking about the yield values obtained, the optimum waste to lignite ratio was found to be 1:1. Furthermore, the result might suggest that manure works as a hydrogen donor solvent for lignite under this environment, as was revealed in previous studies [6-8, 12]. Moreover, to get higher value light products and steady heavy products, manure can be used in the liquefaction of coal [24]. Conversely, using more biomass can reduce the conversion of important products from coal [3].

#### 4. Conclusions

The results of liquefaction experiments summarized below:

- The liquefaction yields attained from the liquefaction of EL and waste material mixture are very high, specifically, when compared with the OG yields from the liquefaction of lignite alone.
- Increasing the manure portion raised total conversion, this outcome supports the using of biomass as a hydrogen donor.
- The “liquid to solid” ratio was 3:1, and the “waste to lignite” ratio was 1:1.

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