

Hydro Liquefaction of Pakistani Coal in Benzene Yields of Liquefied Products as Function of Operating Conditions

I. AHMAD * AND M.A. KHAN

*Department of Chemistry
University of Peshawar, Pakistan*

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Summary: Degari coal was liquefied in a micro reactor in benzene. Yields of liquefied products as a function of operating conditions were calculated. Liquefaction was performed under varying conditions of temperature, hydrogen pressure, residence time, coal/solvent ratio and coal particle size. Maximum conversion of the coal under study to liquid products has been observed at temperature of 400°C, residence time of 1 hour, hydrogen pressure (cold) of 15 kg/cm², coal/solvent ratio of 1:2 and coal particle size of 250-212 μ m. Benzene proved to be an effective solvent for obtaining reasonable yields of liquefied products.

Introduction

Coal had enjoyed popularity as major source of energy since the early industrial development till discovery of huge reserves of petroleum oil in the Arab Peninsula. Subsequent to these discoveries, the use of coal lost its importance in the energy scene because of cheap and easily available supplies of petroleum based oils. The heavily dependence of the world energy sector on these oils has led to a progressive oil shortage. Moreover, the Arab oil embargo of 1970 has paved the way for re emergence of coal as a major source of energy for power generation and blast furnace operations.

Conversion of coal into liquid hydrocarbons has also become an active area of research [1-5]. This renewed interest in coal has necessitated a better understanding of the processes involved. Liquid fuels from coal could be a future alternative to conventional petroleum. Hydroliquefaction of coal in some solvent has been reported elsewhere [6-7], however, these processes are not cost effective. If cost would become competitive, coal could be the future source of liquid fuels [8].

The present work deals with the conversion of Pakistani coal to liquid products using Benzene as solvent under varying condition of temperature, hydrogen pressure, residence time, coal solvent ratio and coal particle size. The objective was to optimize reaction conditions and to make the process cost effective.

Results and Discussion

Effect of Temperature

Content of liquefied products i.e. TLP, PI and PS as a function of reaction temperature is provided in Fig. 1. It is evident from the compiled results that the yields are quite low at low temperature & have progressively increased with the increase in temperature. Yields of total liquefied products were 36.46, 29.97, 18.23, 13.52, 11.66, and 11.60 %, yields of asphaltenes obtained were 1.7, 3.5, 3.9, 1.5, 1.6, and 2.8 % and the yields of desirable products i.e. oils and volatiles found were 34.72, 26.44, 14.30, 11.93, 10.04 and 8.73 % obtained at 450, 400, 350, 300, 250, and 200°C respectively. 450°C was found the optimum temperature for maximum conversion of coal under study into desirable products.

One can think about several explanations for this dependence of yields on temperature, however the one that springs in to mind is that coal believed to be a three dimensional aromatic lamellae of monomers, these monomers are connected with each other by weak linkages like etheric, methylene, propylene etc. At low temperature, these linkages remain in tact. When the temperature is increased, these linkages start scission due to thermal shock, get cleaved leading to free radicals formation which are converted by hydrogen capping reactions to liquid products [9]. If the temperature is further increased, the liquefied products are themselves thermally cleaved leading to dehydrogenation reaction, which are mainly gas forming reactions. The results are in good agreement with this proposition.

*To whom all correspondence should be addressed.

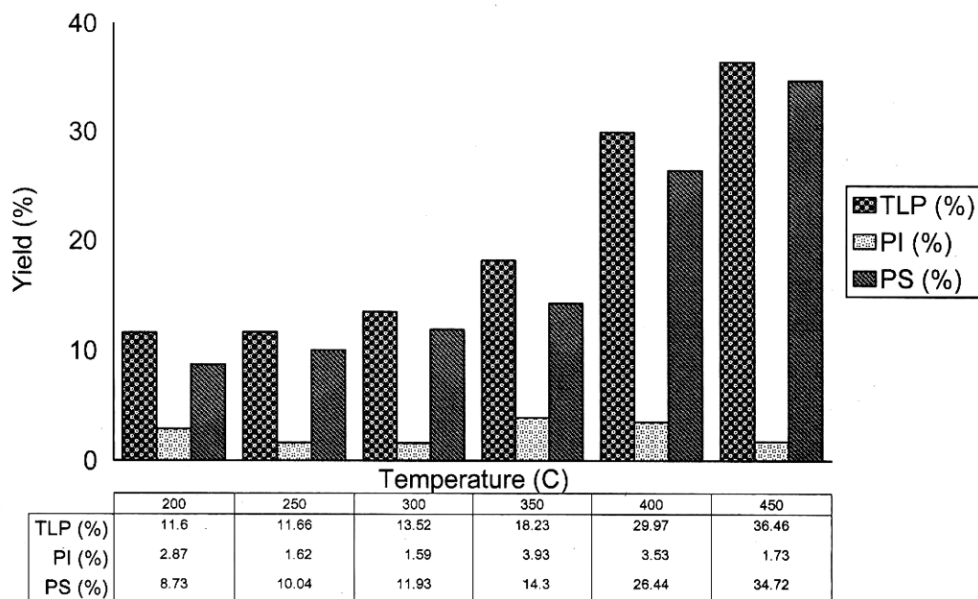


Fig. 1: Content of TLP (Total Liquid Products), Pentane Soluble) and PI (Pentane Insoluble) as Function of Temperature. Residence time of 0.5 hr. Hydrogen Pressure 15 kgf/cm², Coal-Solvent Ratio (1:4), Stirring Rate (250-350 rpm), Solvent: Benzene, Coal Particle Size: 250-212 μ m.

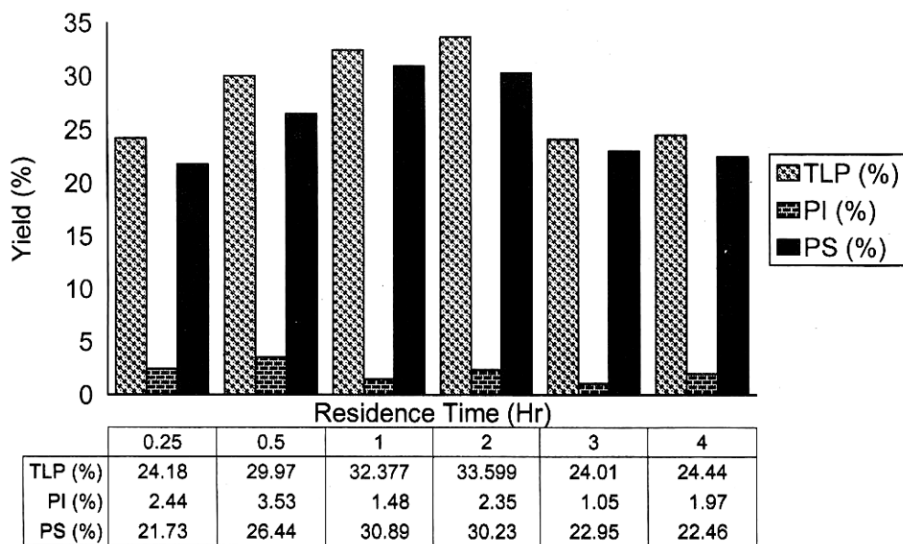


Fig. 2: Content of TLP (Total Liquid Products), PS (Pentane Soluble) and PI (Pentane Insoluble) as Function of Residence Time at Temperature 400°C, Hydrogen Pressure 15 kgf/cm², Coal-Solvent Ratio (1:4), Stirring Rate (250-350 rpm), Solvent: Benzene, Coal Particle Size: 250-212 μ m.

Effect of Residence Time

The time required for the free radicals to be entrapped by hydrogen and converted to liquid product is the residence or contact time. Content of liquefied product as a function of residence or contact time is provided in Fig. 2. The percentage yields of total liquid products were 24.18, 29.97, 32.37, 33.59, 24.01, and 24.44%, asphaltenes were 2.449, 3.5, 1.4, 2.35, 1.05, 1.9 %, oils and volatiles were 21.732, 26.44, 30.89, 30.23, 22.95, and 22.46 % obtained at residence time of 0.25, 0.5, 1.0, 2.0, 3.0, and 4.0 hrs respectively. It can be seen that 1-hour time is optimum for maximum conversion of coal into desirable liquid products. Extension of time has no positive effect on the yield pattern. It can be seen that extension of time has deleterious effect. This may be attributed to the fact of thermal cleavages of the end products. The only advantage of the extension in time, which can be noticed, is the decline in asphaltene contents. Asphaltenes are giant molecules and are pentane insoluble fractions. The low yield at reaction time less than one hour is attributed to the fact of the free radicals formation. At time less than one-hour, free radical formation and their capping in a pool of hydrogen is less excessive thus causing low yields. Decline in yields upon extension in time more than one hour might corresponds to the onset of retrogressive reactions which are mainly coke forming [10].

Effect of Hydrogen Pressure

Gas phase reactions or depolymerization reactions in a hydrogen environment favore at high pressure as enunciated by Hennery's law. The content of liquefied products as a function of hydrogen pressure is provided in Fig. 3. The yields of total liquefied products were 29.97, 31.337, 35.380, and 36.973%, asphaltenes were 3.53, 2.41, 1.58, and 2.80, oils and volatiles were 26.44, 28.96, 33.79, and 34.17 % obtained at 15.0, 20.0, 25.0, and 30.0 Kg/cm². It can be seen a marked effect of hydrogen pressure on the product yields. The reason might be good contact of partners at the reaction sites. More over high hydrogen pressure inhibits dehydrogenation reactions, which are mainly gas forming reactions [11,12]. The other reason sprinkled into mind is the imbibition. Benzene has the ability to imbibe into coal effectively [13]. This imbibition could be increased by increasing the pressure as well as high pressure makes sure the availability of the pool hydrogen for effective recapping of the thermally generated free radicals.

Effect of Coal/Solvent Ratio

Graph of Content of liquefied products as a function of coal/solvent ratio is provided in Fig. 4. Yields of total liquefied products found were 35.17, 35.91, 29.45, 29.61, 29.12, 29.52, and 29.97 %,.

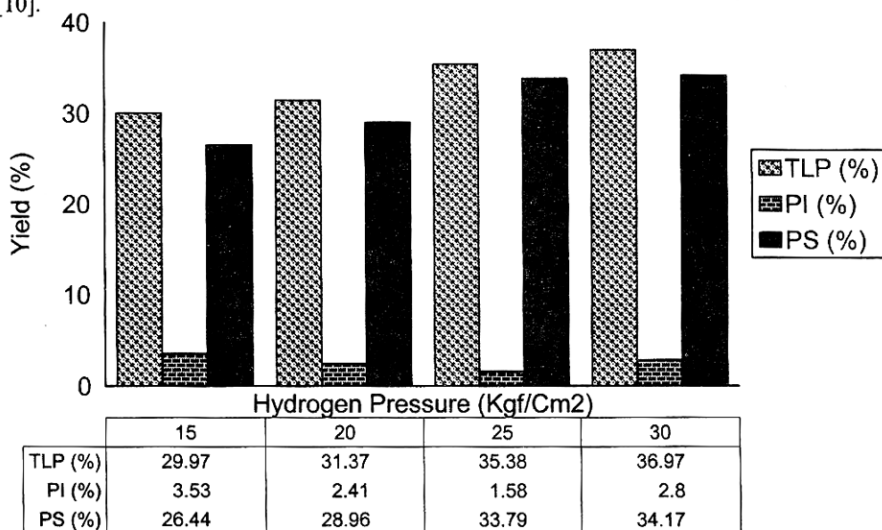


Fig. 3: Content of TLP (Total Liquid Products), PS (Pentane Soluble) and PI (Pentane Insoluble) as Function Hydrogen Pressure. Temperature 400°C Residence Time 0.5 hr. Coal-Solvent Ratio (1:4), Stirring Rate (250-350 rpm), Solvent: Benzene, Coal Particle Size: 250-212 μ m.

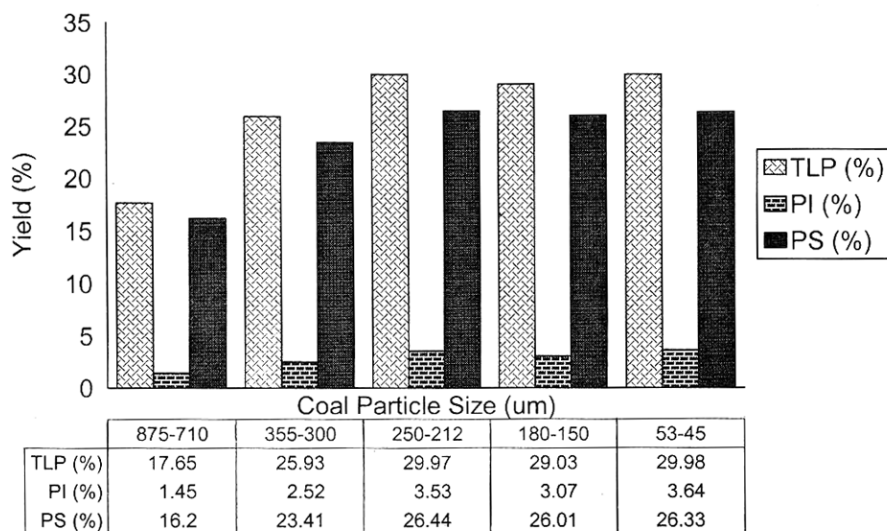


Fig. 4: Content of TLP (Total Liquid Products), Pentane Soluble) and PI (Pentane Insoluble) as Function of Coal Particle Size Temperature 400°C Residence Time 0.5 hr. Hydrogen Pressure 15 kgf/cm² Coal-Solvent Ratio (1:4), Stirring rate (250-350 rpm), Solvent: Benzene.

asphaltenes were 0.65, 0.25, 1.03, 0.76, 1.46, 2.14, and 3.53 %, and oils and volatiles were 34.52, 35.66, 28.41, 28.85, 27.66, 27.38, and 26.44 % obtained at 1:1, 1:2, 1:4, 1:5, 1:6, 1:10, and 1:20 coal/solvent ratio respectively. A noticeable effect can be seen. Coal/solvent ratio of 1:2 was found to be optimum. The increase or decrease in coal/solvent ratio has a negative effect on the yield pattern. The reason might be good heat transfer, effective solvation, no retrogressive reactions, effective hydrogen and recapping activities favored at coal/solvent ratio of 1:2.

Effect of Coal Particle Size

The effect of particle size on the yield of liquefied products can be seen from the data compiled in Fig. 5. Yields of total liquefied products were 17.65, 25.93, 29.97, 29.09, and 29.98 %, asphaltenes were 1.4, 2.5, 3.53, 3.07, and 3.64 %, and oils and volatiles were 16.20, 23.41, 26.44, 26.01, and 26.33 % obtained using coal samples of particle size range 850-710, 355-300, 250-212, 180-150, and 53-45 μm . From the yield pattern, one can assimilate about the enhancement in yields upon particle size reduction. This enhancement might be due to the intimate contact between the reaction sites. Another reason as we have already reported in our earlier paper, is the role of coal minerals. Pyrite, which is

abundantly present in coal and its role as a catalyst in liquefaction studies of coal has been underlined previously [14]. Guin *et al* [15] have reported that smaller size pyrite was more catalytically active than larger size pyrite. Granoff and Baca [16] have correlated the H/C ratio of the liquid product to the particle size of pyrite. The hypothesis of effect of particle size on conversion was also confirmed by Stohl and Granoff [17]. There are also evidences of pyrite conversion to pyrrhotite [17] during liquefaction and this conversion is mostly favored as size of pyrite decreases. The enhancement in yields might correspond to the high pyritic content of the coal under study.

Experimental

Coal Samples

The coal sample was obtained from Degari Coal Mine through PMDC (Pakistan Mineral Development Corporation). It was preliminary crushed using a pistol and mortar. The crushed sample was screened to desired particle size portions using a mechanical sieve shaker. These portions were dried in an oven at 105°C to constant weight and then used. The proximate and ultimate analysis of the coal used is provided in Table-1.

Table 1. Proximate and Elemental Analysis (%) of Degari Coal

Proximate Analysis				Ultimate/ Elemental Analysis				
Mois- ture	VM	Ash	FC	C	H	S	Cl	Calorific Value (cal/gm)
12.1	35.5	18.0	34.4	50.9	4.2	2.2	0.02	8326

Liquefaction Procedure

Liquefaction was carried out in a 1000 ml stainless steel autoclave (OSK-6505) equipped with a mange drive, motor driven stirrer, thermocouple, sensitive pressure gauge, inlet and outlet caps for charging and discharging of gas, safety valve; housed in an electrically heated furnace, and controlled from an operator console. 10-gram portion of already prepared dried coal was slurried in a solvent in a pyrex brand glass vessel inserted tightly in the autoclave. The autoclave was then pressurized to 15 Kg f/cm² with cold H₂ and heated at 5°C min⁻¹ to desired temperature and held there for specified time duration, cooled over night to ambient temperature and depressurized. Liquefied fraction along with solvent was collected and the cake (residual coal) was subsequently sox let - extracted with THF till clearance in the thimble compartment. The extract

from this treatment was combined with the liquid fraction and solvent. The solvent was removed using rotavapour. The extract was collected and separated into *n*-pentane solubles (PS) and *n*-pentane insolubles (PI). The residual coal from the thimble was dried in a vacuum oven at 70°C till constant weight and weighed to calculate percent conversion. TLP (total liquid product) was separated into four fractions according to their solubility in *n*-pentane and tetra hydrofuran. Liquid product was heated on a steam bath for a few minutes in order to obtain a uniform solution of appropriate fluidity. 30 ml of *n*-pentane was then added to it, and shaken vigorously. The asphaltene was precipitated with *n*-pentane, filtered and the filtrate was collected as oil. The residual asphaltene was washed with another portion of *n*-pentane and then dried for 30 minutes at 50°C in a vacuum oven, cooled and weighed. The fractions obtained are listed below together with their solubility characteristics.

Total liquid product	soluble in THF
Asphaltene	insoluble in <i>n</i> -pentane, soluble in THF
Oil	soluble in <i>n</i> -pentane, soluble in THF
Residue	insoluble in <i>n</i> -pentane, insoluble in THF

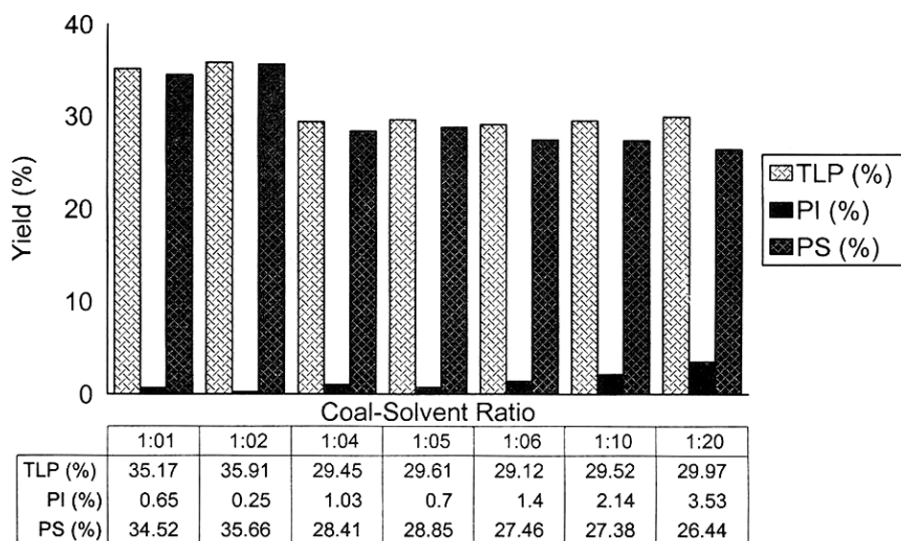


Fig. 5: Content of TLP (Total Liquid Products), Pentane Soluble) and PI (Pentane Insoluble) as Function of Coal Particle Size Temperature 400°C Residence Time 0.5 hr. Hydrogen Pressure 15 kgf/cm² (1:4), Stirring Rate (250-350 rpm), Solvent: Benzene. Coal Particle Size: 250-212 µm.

The calculations were made as:

$$\% \text{ Conversion} = \frac{(\text{Original coal} - \text{residual coal}) \times 100}{\text{Original coal}}$$

Asphaltene was calculated from the weight of *n*-pentane insoluble fraction. Oil and volatiles were calculated as;

$$O (\%) = 100 - A - R.$$

Where

A = weight percentage of asphaltene.

R = weight percentage of residue.

Residue was calculated from the weight of THF insoluble.

$$R (\%) = 100 - A - O$$

Where

A = weight percentage of asphaltene.

O = weight percentage of oil and volatiles.

Conclusions

It can be concluded from this study that the coal under study could be converted into liquefied products. Yields of liquefied products have been found to be dependent on operating conditions. The parameters like temperature, 450°C; residence time, 1.0 hr; hydrogen pressure, 30.0 kgf/cm²; coal/solvent ratio, 1:2; and coal particle size, 250-212 µm were found optimum.

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