

## Thermochemical Liquefaction of Coal

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### Abstract

This paper presents a review of various methods coal liquefaction processes; they can be a result of pyrolysis, solvent extraction, direct or indirect coal liquefaction. Bituminous coals are considered to be the most favorite feed-stock for liquefaction, because of their high yield of liquid hydrocarbon products. The direct coal liquefaction process is more energy efficient than the indirect liquefaction process but is much harder to control. Thermal hydro-cracking of lignin bounds to produce intermediates which then react further with coal producing lower molecular weight material, which more desirable. Enhancement of coal conversion due to the addition of lignin is found to be a function of time. It is dependent upon temperature of reaction and the type of lignin used. By increasing the ratio of lignin to coal will result in depolymerizing larger portions of coal. This finding is proposed in reaction pathway.

**Keywords:** Coal, Liquefaction, Depolymerization, Pyrolysis, Gasification

### 1. Introduction

For more than 200 years ago, and since the beginning of the industrial revolution, coal was the world's main source of energy. Previously, coal derived liquids were mainly by-products of the coke manufacturing industry and used as feedstock for the production of most chemicals [1, 2]. For the past few decades, petroleum has become the primary source for liquid fuels and chemical feedstock. It is becoming more obvious that petroleum reserves are declining, while coal reserves are still abundant. Coal reserves represent about 70% of world's total energy reserves. Coal is considered a solid fossil fuel that can be converted into liquid fuel by the process of hydrogenation [3]. One method used to hydrogenate coal is to subject it to high temperature reaction (or depolymerization) with a hydrogen donor solvent such as tetralin. For an efficient coal depolymerization process, cleavage of selective coal fragments is necessary. While thermal cracking is non-selective and requires high temperature, catalytic cracking can accomplish cleavage at less severe conditions of reaction temperature and pressure. For example, triflic acid (tri-fluoro-methane-sulfonic acid) and iodine are good coal conversion catalysts; para-toluene-sulfonic acid is another catalyst that has been used. Also, coal can be depolymerized in phenol at high temperatures (higher than 425 °C), or at lower temperatures (e.g., 100 °C) using a catalyst such as BF<sub>3</sub>. It is postulated that selective bond cleavage reactions will occur at lower depolymerization temperatures (around 300 °C), which would promote a more efficient use of hydrogen and help different hydrogenation and hydro-cracking reactions to be identified.

### 2. Chemical Coal Structure

Understanding the behavior of coal processing, such as liquefaction, requires a good understanding of its chemical structure. Coal is an insoluble, black, amorphous, non-homogenous solid material that contains wide range of structural groups and a good population of free radicals. It is considered to be a complex macromolecular network system, which contains two major phases. One phase is inorganic and made up mainly of mineral matter; mineral matter in coal complicates the chemical treatment of coal. It has adverse effects of commercial coal utilization, such as paying for the shipment of mineral matter in coal and the problem of ash disposal following coal processing. The other phase is organic and made up of macerals. The high molecular weight material of coal can be converted into liquid fuel, with lower molecular weight, by bond breaking reactions. Coal was formed by metamorphosis of accumulated plant remains in swamps under anaerobic conditions. It consists of a number of macerals: (a) Vitrinite, which is considered to be the principal segment of bituminous coals, especially those with relatively high OH contents [4]. They are derived from lignin, which controls the coking behavior and yield of phenolic compounds. Vitrinite can have high volatility content. (b) Exinite (or liptinite), which is considered the most volatile constituent, and was derived from algae, resins and spores. (c) Intertinite, which is the most condensed maceral, almost charcoal-like in its non-fusible character, but can be soluble in certain solvents. It has low volatility content. The level of reactivity of the above three groups is different from one coal to another and varies with

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rank. Coal is one of the most complex organic materials whose structure and reactivity have been systematically studied. Considering the postulated structure of the bituminous coal given in Fig. 1, it is seen that the building blocks are primarily aromatic and hydro-aromatic. According to Walker [5], the amount of aromatic to hydro-aromatic character will vary with the rank of coal. At the edges of the building blocks, there are hetero-atoms (i.e., oxygen, sulfur, hydrogen, and nitrogen), which are liberated during heat-treatment of the coal at high temperatures. Cross-links exist in the coal; one is the methylene cross-link, the other is the oxygen-ether cross-link. As the number of cross-links increases, the apparent molecular weight of the coal increases. The coal will change from a thermoplastic material, which softens upon heating, to a thermosetting material as the number of cross-links in the original coal increases, and as the number of cross-links formed during heat-treatment increases.

Compared to petroleum, coal is found to be hydrogen deficient. It also contains a lot more oxygen, nitrogen, and ash. At today's prices coal cannot be considered the most attractive energy source when compared to petroleum and natural gas. However, petroleum is on the rise for the past few years (see Fig. 2). Most plants use petroleum or natural gas, whereas coal has not reached that level yet. The reason is because of the enormous high capital cost associated with coal-based plants, as well as the fact that prices of coal liquid fuels are still unattractive [6]. However, coal will eventually become the world's main source of fuel and chemical feedstock because of the depletion of oil and natural gas. Transitions of the main source to coal will not occur quickly, and will very much depend on economic and political reasons. The technology for the production of chemicals from coal already exists. As the world's oil supplies become scarce and the improved coal technology starts to emerge, the commercialization of such technologies will increase.

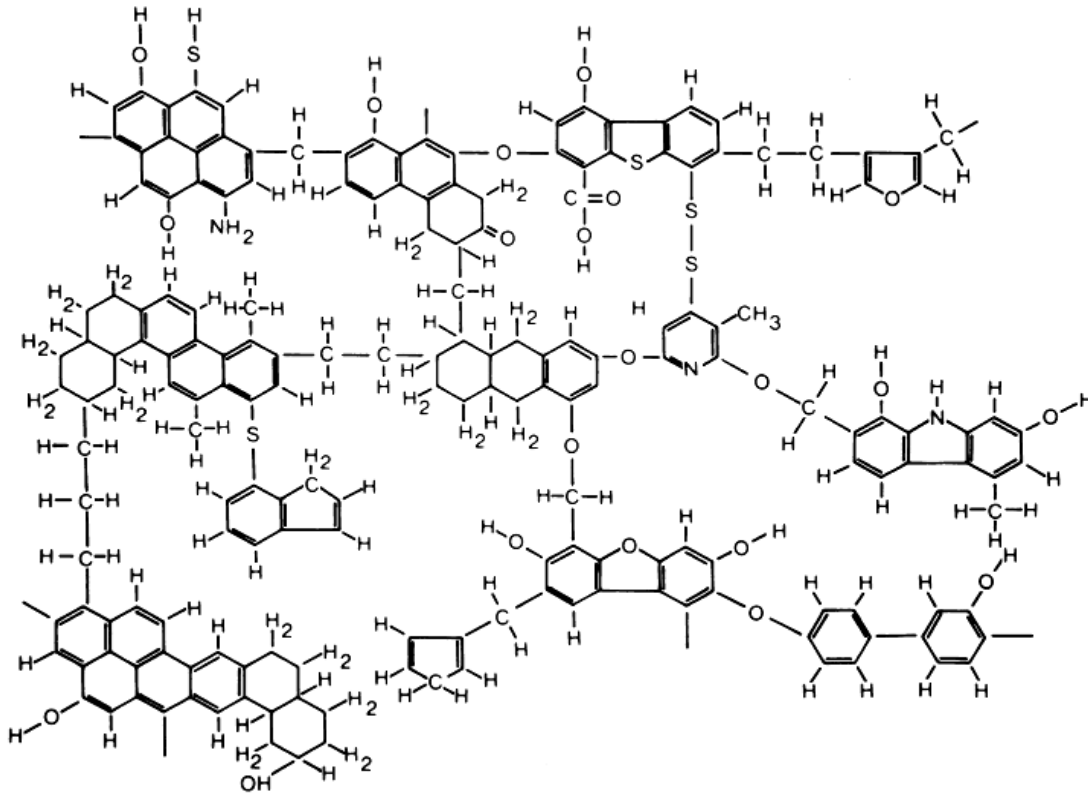


Fig. 1 Bituminous coal Structure

### 3. Coal Utilization

Since the 1980s, a new generation of coal technologies has emerged in the USA, Europe, and different parts of the world. These new technologies have the potential to produce energy with high efficiency, and make a coal-fired plant burn as clean as natural gas, the cleanest fossil fuel. They can be installed at various stages in the fuel chain or used to convert coal into other more efficient and environmentally sound form of fuel. They can be divided into two major categories. One at which energy is liberated directly as follows:

- Pre-combustion: Sulfur, methane and other impurities can be removed at an earlier stage, before coal reaches the boiler. Two traditional approaches, physical and chemical cleaning, have been used, as well as biological cleaning, which employs microbial and enzymatic techniques to liberate sulfur and ash.
- Combustion: Fluidized bed combustion and advanced slagging combustion. The pollutants are removed as coal is fired.
- Post-combustion: Flue gases are cleaned as they exit before they are sent out the smoke stack.

The other category is coal conversion into other form of fuels. They are divided into different types of processes as follows:

- a) Gasification: Coal is broken into gaseous molecules at high temperature, in the presence of air or steam. The gases are purified and the clean gases are burned. Also, steam and electricity are usually produced in such processes.
- b) Mild gasification: Gaseous, liquid, and solid fuels are produced in this type of process. Coal is heated in an oxygen free environment at lower temperatures.
- c) Fuel cells: Gasified coal is used as a source of hydrogen to supply the fuel cell for an electrochemical reaction. During this reaction, oxygen and hydrogen atoms are combined to form water and thus energy is released.
- d) Magnetohydrodynamics (MHD): Coal is fired at about 3000 K. At this temperature the products of combustion are sufficiently ionized to have an appreciable electric conductivity. The degree of ionization can be increased about one-hundredfold by adding 1% potassium or cesium. The combustion is usually carried out at 0.5 to 1.0 MPa. The hot gases can be expanded at high velocity through a nozzle transverse to magnetic field resulting in generation of an electric current in the gases that flows at right angles to the direction of both the high velocity gas flow and the magnetic field. Thus the turbine and generator are not required and the temperature limitations of the gas turbine can be avoided.
- e) Coal liquefaction: Coal is converted into liquid fuel either directly or indirectly. The following sections describe coal liquefaction in more detail.

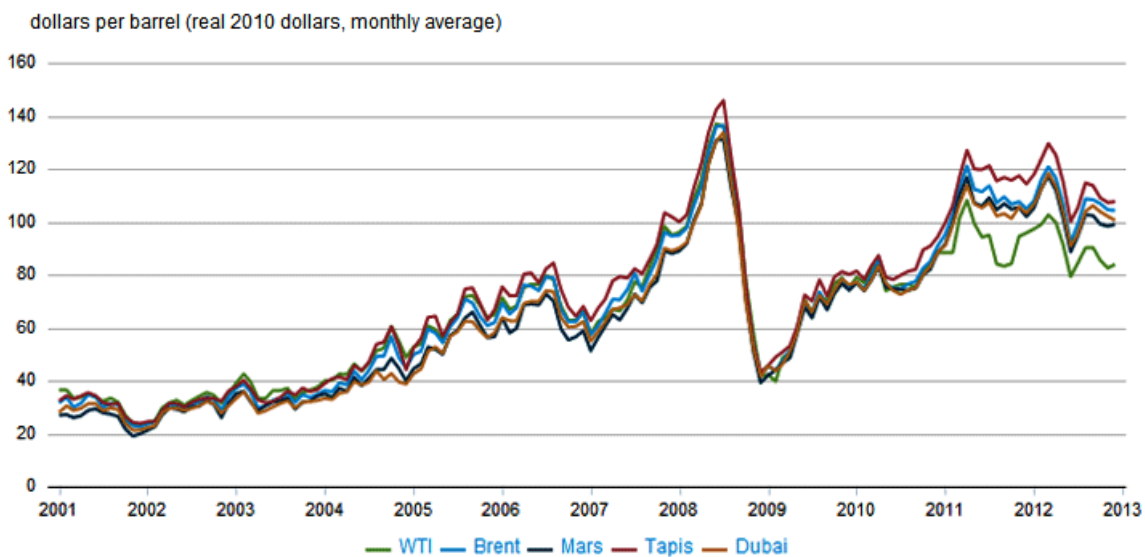


Fig. 2 World crude oil prices for the past 12 years (source: [www.eia.gov/finance/markets/images/world\\_oil\\_prices.png](http://www.eia.gov/finance/markets/images/world_oil_prices.png))

#### 4. Coal Liquefaction Processes

Coal liquefaction is considered to be an important option among other technologies, such as enhanced oil recovery, more severe oil processing, shale oil, and tar sand. Coal liquids are produced by four major types of processes:

- a) Pyrolysis
- b) Solvent extraction
- c) Indirect liquefaction
- d) Direct liquefaction

The main objective of coal liquefaction is to manufacture premium liquid fuels from coal. The liquid fuels may directly be substituted for those fuels obtained from petroleum. This would allow the continuing use of already existing high performance engines in a post petroleum era.

##### 4.1. Pyrolysis

When coal is heated to high temperatures (500–1000 °C), in an inert environment, then 20 to 40 percent of the original solid is liberated into gas or volatiles. This process is called pyrolysis or devolatilization of coal. The volatiles that are liberated can be a good source for liquid fuels. The liquid products from pyrolysis are characterized to be heavy, thick oils, with almost tar-pitch character. Greater amounts of liquid can be produced by heating the coal at high rate. Also, more liquid with longer chains can be produced if the gaseous volatiles are removed faster from the vicinity of the solid char residue and from the high temperature zone.

##### 4.2. Solvent Extraction

The idea of solvent extraction came about when coal was considered to be a gel which contains a lot of soluble molecules that are fixed by van der Waals forces in an insoluble matrix. In a relatively high temperature environment

(370–480 °C), the gel matrix can swell and overcome the van der Waals forces allowing the soluble material to be extracted. A non-hydrogen-donor solvent is used, such as anthracene oil, in the absence of hydrogen.

### 4.3. Indirect Liquefaction

The idea of indirect coal liquefaction process is to convert coal into a synthesis gas mixture of hydrogen and carbon monoxide. The synthesis gas is then recombined forming a long-chain liquid fuel. In the initial step, coal is gasified in a high pressure gasifier. It is reacted with steam and oxygen (air) at high temperature, forming hydrogen and carbon monoxide. The following step is the purifying and cleaning up of the synthesis gas. The purified gas is then reacted (i.e., combined in the presence of a catalyst) in a liquefier to form the desired final hydrocarbon liquid product.

### 4.4. Direct Liquefaction

The goal of direct coal liquefaction is to break down the coal's large hydrocarbon molecular structure into smaller molecules. The smaller molecules must be associated with liquid hydrocarbons, in addition to minimizing the very small molecules associated with hydrocarbon gases (e.g., methane and ethane gases). The conversion of coal to liquid requires the addition of hydrogen gas. High temperatures are required in such processes.

Coal radicals are produced by thermal cleavage of ether bonds during coal liquefaction. These radicals react with hydro-aromatic structures to produce cyclohexadienyl radicals. Cyclohexadienyl radicals can also be formed by the reaction of aromatic and hydroaromatic structures. The formation of the "cyclo" radicals will lead them to react with a variety of substituted aromatic and phenol ring systems. The outcome of such reaction pathway will be an expulsion of a fragment leading to reduction in molecular size of the coal material and the formation of aromatic rings from cyclohexadienyl radicals. The newly formed aromatic rings can thus react with more hydroaromatic rings until exhaustion.

Bituminous coals are considered to be the most favorite feedstock for liquefaction, because of their high yield of liquid hydrocarbon products. The direct coal liquefaction process is more energy efficient than the indirect liquefaction process but is much harder to control. A catalyst is usually used as a reaction promoter. Inexpensive and readily recoverable catalysts are preferred, but at the same time, it is important to produce a higher quality liquid product at lower severity conditions.

## 5. Recent Developments in Coal Liquefaction

Depolymerization or thermal cleavage of chemical bonds of coal was studied by Neavel [7]. Formation of free radicals from coal was observed. The stabilization of these radicals with hydrogen is necessary, in order to avoid repolymerization of the free radicals. Hydrogen may be abstracted from hydrogen donor solvent such as tetralin. During such process tetralin is first converted into dihydronaphthalene and then to naphthalene. The reactions are shown in Figures 3 to 5. Fig. 3 depicts the donation of four hydrogen atoms for each tetralin molecule, while the formation of free radicals from the coal structure is presented in Fig. 4. The stabilization of these free radicals into lower molecular weight compounds is shown in

Fig. 5. Tetralin was extensively used in many coal liquefaction studies [8].

Skowronski and Heredy [9] investigated the liquefaction of bituminous coals without the addition of any kind of hydrogen-donor solvent. Hydrogen was applied directly to dry coal under moderate thermal depolymerization conditions. Lower rank bituminous coal was more reactive and produced higher yields than the higher rank coals. Higher conversions of bituminous coal were obtained by Mikita et al [10] by using water or non-hydrogen-donor vehicles (e.g., cyclododecane) as a suitable liquefaction media. Reactions were carried out in micro-reactors with little or no hydrogen-donor solvents at moderate thermal conditions (385 °C), and under high hydrogen pressure (1200 psi cold). It was suggested that the analyses of coal derived liquids are easier to obtain without the interference of solvent. The conversions at such conditions were higher than those with the dry hydrogenation process.

High and low ranks of coals were able to be depolymerized in phenol, at a reaction temperature of about 400 °C [11]. It was observed that the depolymerization was accompanied by extensive rearrangements of hydrogen; the liquid product was very low in hydrogen content. At lower temperature (e.g., 100 °C) bituminous coal can be depolymerized in phenol, too. It was found that the extent of depolymerization would triple its pyridine solubility value, from about 20 to 60 percent, upon the addition of BF<sub>3</sub> to the reaction mixture.

Coal liquefaction using binary solvent systems has been studied [12]. Coal was liquefied using tetralin and polynuclear aromatic compounds such as fluorine, phenanthrene, 1-methyl-naphthalene, or naphthalene. The hydrogen-transfer reaction from tetralin was accelerated by the addition of fluorine or phenanthrene, and thus produced high conversions. Coal conversion was not as high as when the other mixture of 1-methyl-naphthalene or naphthalene with tetralin was used. An enhancement in coal conversion was also reported upon the reaction with a mixture of indene with tetralin or decalin [13, 14]. It was confirmed that indene oligomers acted as hydrogen donors. The hydrogen abstraction reaction of the hydrogenated indene oligomer from decalin is a result of this synergistic effect [12]. For higher rank coal this observation did not occur [15], but with the mixture of tetralin and 1-methyl-naphthalene, higher coal conversion was observed. 1-methyl-naphthalene is known to be a non-hydrogen-donor compound. In another study the reaction of coal and n-butylamine was carried out at low temperatures (less than 300 °C). Coal conversions were found to be higher than those conversions using tetralin. At higher temperatures the opposite occurred. It was found that undesirable condensation or polymerization reactions of coal fragments can occur. Decalin is another solvent that has been studied as a substitute for tetralin in coal liquefaction.

Chemical pretreatment of coal prior to liquefaction was investigated [16]. Alkylation of coal was found to be a beneficial pretreatment step for the enhancement in coal conversion during coal liquefaction. The largest enhancement was obtained at low severity conditions, for lower rank coals. An oxygen-selective alkylation procedure was used. It was found to be effective for the low rank subbituminous coal under identical reaction conditions. Non-selective methylation did not show any enhancement for the low rank coal (Wydok subbituminous coal), but it was effective for high rank coal (Illinois bituminous) at higher severity conditions. Liquefaction of coals pre-swollen in acetone has shown increase in the hexane soluble fraction of the final liquid product. In another study higher yields and product quality were obtained upon

pre-swelling of coals. The most effective swelling agent was found to be tetrabutylammonium hydroxide [17]. Methanol and tetrahydrofuran were also found to be better effective swelling agents for bituminous coal conversion.

Addition of iodomethane resulted in substantial yields of products in a study by Vassalo et al [18]. An increase in the aromatically and methyl content of bituminous coal was

observed when it was treated with iodomethane at 300 C. methyl groups from iodomethane are captured by aromatic rings in the coal, and hydrogen is removed from hydroaromatic structures by the same reagent [19]. Other work concerning the area of coal liquefaction based on coal model compounds [20], or catalytic coal liquefaction was presented in literature.

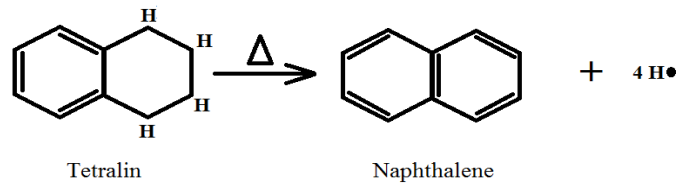


Fig. 3 Chemical reactions showing the donation of four hydrogen atoms for each tetralin molecule

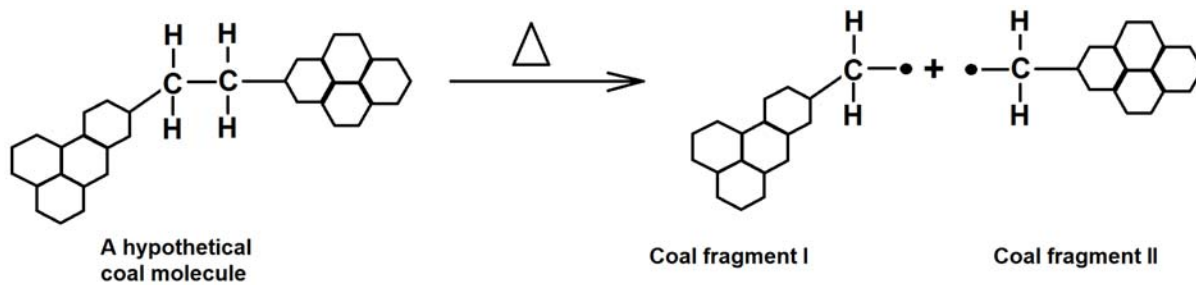


Fig. 4 Chemical reactions showing the formation of free radicals

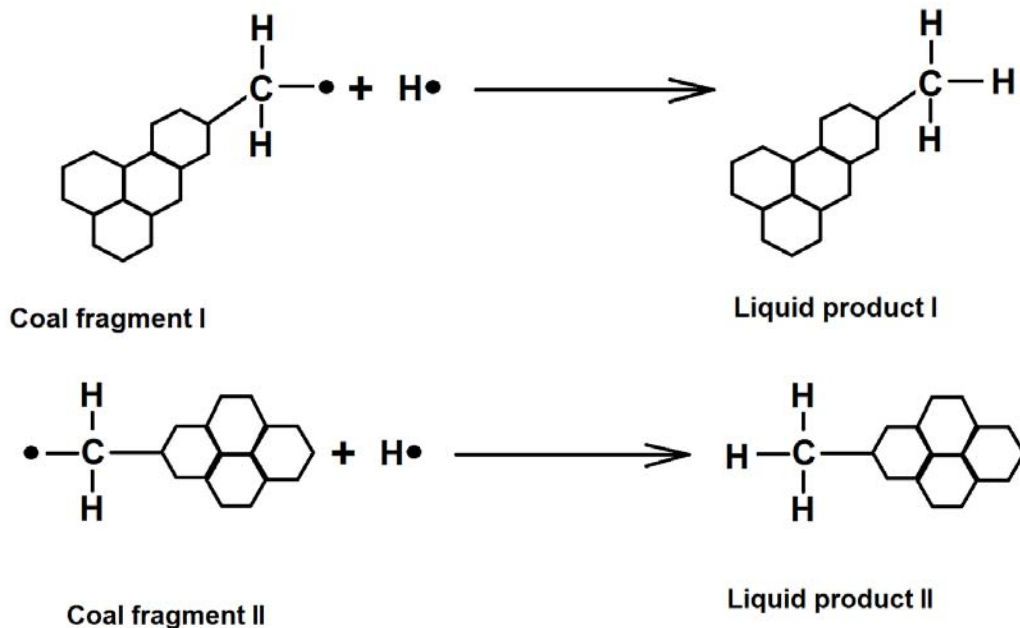


Fig. 5 Chemical reactions showing the stabilization of free radicals by reacting with hydrogen forming smaller molecular weight compounds

## 6. Coprocessing of Coal with Other Materials

Depolymerization of coal by phenolation was presented. A technique was developed for the depolymerization of coal using  $\text{BF}_3$  catalyst in phenol at  $100\text{ }^\circ\text{C}$  in which the coal was acting as an alkylating agent [21]. Similar reactions were reported using *p*-toluenesulfonic acid as a catalyst [22]. Other studies reported that certain non-phenolic solvents such as xylenes are also able to enhance the solubility of coal through depolymerization reactions [23]. Larsen et al reported that heating coal in phenol to  $425\text{ }^\circ\text{C}$  caused a depolymerization accomplished by extensive rearrangement of hydrogen to produce a hydrogen-rich soluble fraction and hydrogen-poor insoluble residue [11]. Later, Larsen et al reported that the amount of colloidal material present in coal extracts from those depolymerization reactions is large [24]. It was attributed the failure of phenol-acid depolymerization of coal to the fact that bonds cleaved under the reaction condition are not plentiful and that acid-catalyzed condensation reactions take place.

Co-liquefaction of coal with polypropylene or polystyrene in hot compressed water was conducted [25-27]. Also, other studies considered addition of saw dust [28-30].

Thermal decomposition of 2,2'-dinaphthyl ether, phenol-benzyl ether and dibenzyl ether are significantly accelerated in the presence of phenols [31]. Other studies have shown that the reactions of the three atom linkages are promoted by free radical initiators such as phenoxy and benzyl radicals [32]. Consequently, both phenolic compounds and compounds that can generate free radicals very rapidly improve the conversion of coal to soluble products. The generation of phenoxy radicals and phenols can be predicted to be delivered from lignin during lignin thermolysis.

Lignin has a high content of phenolic components and a prevalence of liable methoxy groups. The inherent resonance stabilization of the phenoxy radicals insure their existence as monomers which can penetrate the coal structure and shuttle hydrogen to hydrogen-poor coal fragments, enhancing coal depolymerization and product stabilization.

Many studies have been directed to understanding the formation of liquid products from coal in the presence of lignin and wood pyrolysis oil [33-41]. It was observed that thermal hydro-cracking of lignin results in the formation of substituted phenoxy radicals, as well as other types of radicals. Fig. 6 shows a typical guaiacyl moiety within the lignin molecule. It contains  $-\text{O}-\text{CH}_3$  and  $-\text{O}-\text{R}$  bonds with low energies. Preferred thermal dissociation of such bonds leads to formation of phenoxy radicals. The formation of these radicals is shown in Fig 7. Such phenoxy radicals will be effective and active intermediates to attack the coal, causing scission of the aliphatic carbon-carbon bonds in the coal. Fig. 8 shows the reaction of the phenoxy radical with coal causing hydrocracking in the coal structure. An overall enhancement in the coal depolymerization and lower molecular weight compounds will be produced.

## 7. Discussion

In order to explain the apparently favorable effects of lignin on depolymerization of coal, it is helpful to consider the following proposed chemical reaction mechanisms:



In the above 3 reactions: *L* and *C* refer to lignin and coal, respectively. Also *I<sub>1</sub>* and *I<sub>2</sub>* refer to intermediate products, while *P<sub>1</sub>*, *P<sub>2</sub>*, and *P<sub>3</sub>* refer to final products, whereas, *k<sub>1</sub>*, *k<sub>2</sub>*, *k<sub>3</sub>*, *k<sub>4</sub>*, and *k<sub>5</sub>* are chemical reaction rate constants. The first two reactions represented by equations (1) and (2) are hypothesized to occur when lignin and coal are alone depolymerized. When lignin is added to coal, the intermediates from reaction (1) further depolymerize coal via reaction (3). The enhancement in coal conversion obtained is due to reaction (3). The concentration of intermediates (*I<sub>1</sub>*) should be dependent on time; it is being zero at the beginning of the reaction and should increase with time as lignin is depolymerized. At a certain time *I<sub>1</sub>* should reach a maximum value after which it starts to decline as it is consumed in reactions (1) and (3). Thus, the enhancement in coal conversion should also increase with increasing *I<sub>1</sub>*, and hence it should reach a maximum value before it declines.

Thermal hydro-liquefaction of coal is believed to proceed by a free radical mechanism. Thermal hydro-cracking of lignin bounds to produce intermediates which then react further with coal producing lower molecular weight material, which more desirable. Enhancement of coal conversion due to the addition of lignin is found to be a function of time. It is dependent upon temperature of reaction and the type of lignin used. It was reported that enhancement in coal conversion was a function of lignin to coal ratio in a coal-lignin mixture when reacted with tetralin [27-35]. By increasing the ratio of lignin to coal can result in depolymerizing larger portions of the coal. The conversion did not improve upon increasing the value of lignin to coal beyond 2.33. This finding is in agreement with the proposed reaction pathway.

In order to verify the hypothesis that addition of lignin is responsible for the enhancement of coal liquefaction in the coal-lignin mixture, an effort was made by reacting coal with lignin-derived liquid. An enhancement in coal conversion was obtained which substantiated the hypothesis that intermediates produced by lignin do react further with coal. The intermediates are short-lived and after some period of time (about 2 hours) their effect of coal depolymerization becomes negligible. The characterization of the liquid products was another indicator that supports this hypothesis. It was found that the liquid produced from coal-lignin mixture contains appreciably lower amounts of the molecular weight benzene insoluble compounds, and higher quantities of the lower molecular weight asphaltene and pentane soluble fractions over the corresponding fractions in liquids obtained by processing the coal or lignin alone without the presence of the other fuel. The formation of the lower molecular weight compounds can be attributed to the formation of radicals which are stabilized by abstracting hydrogen from the hydrogen-donor solvent. Boiling range distribution curves were determined for reaction of coal and lignin in tetralin independently, and reaction of coal and lignin in tetralin combined. The results obtained show that a significantly greater amount of low temperature distillable material is obtained when lignin and coal reacted together as compared to the expected fraction calculated assuming no positive influence

of lignin addition on coal depolymerization. These results were also found to be in agreement with the overall reaction chemistry shown in equations (1) to (3). The liquid products from coal and coal-lignin mixtures were subjected to

accelerated aging environments. The effect of aging was determined by the solubility of the liquids in benzene and by molecular weight characterization. It was found that addition of lignin to coal resulted in more stable compounds.

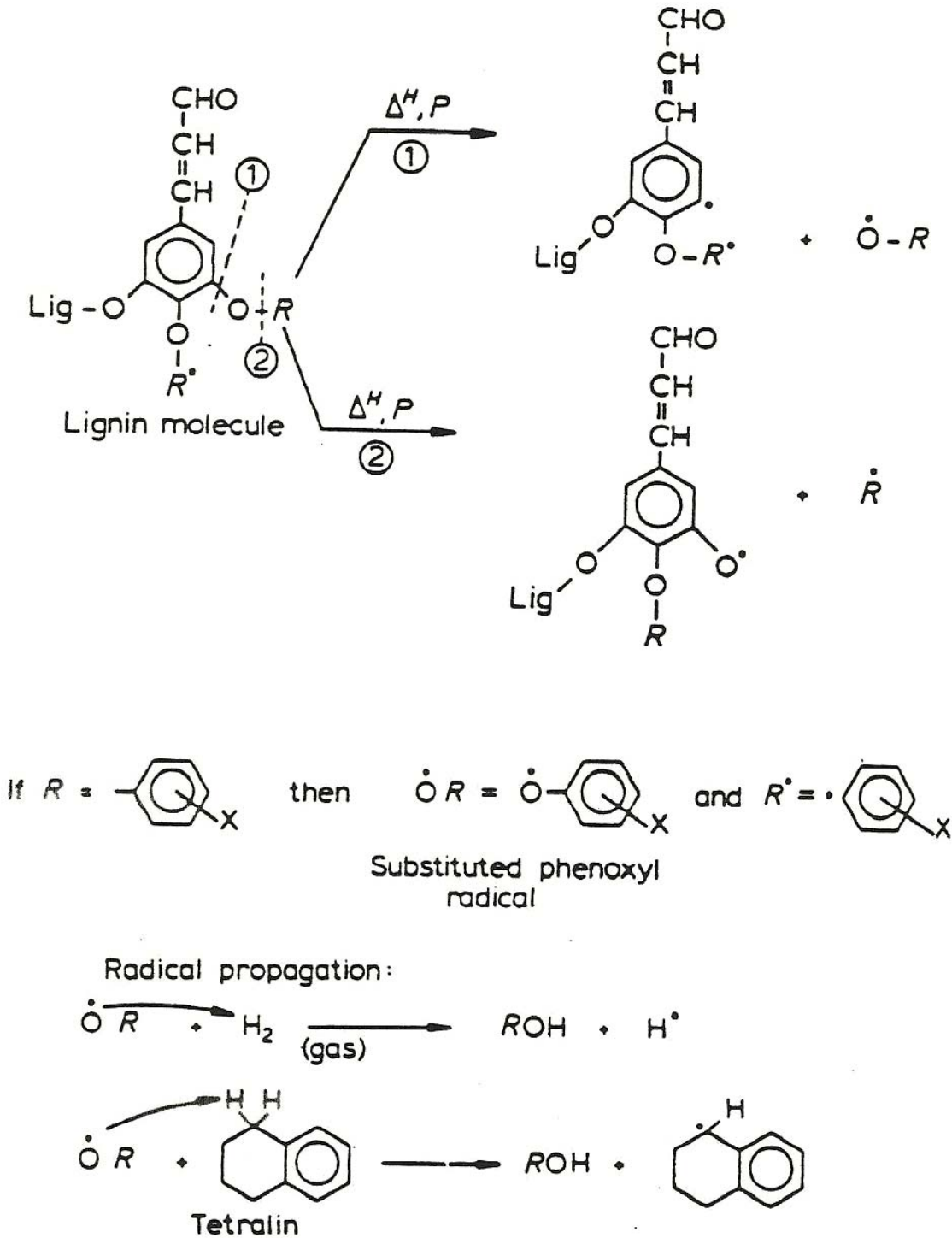


Fig. 7 The formation of phenoxy radicals from thermal hydro-cracking of lignin molecule



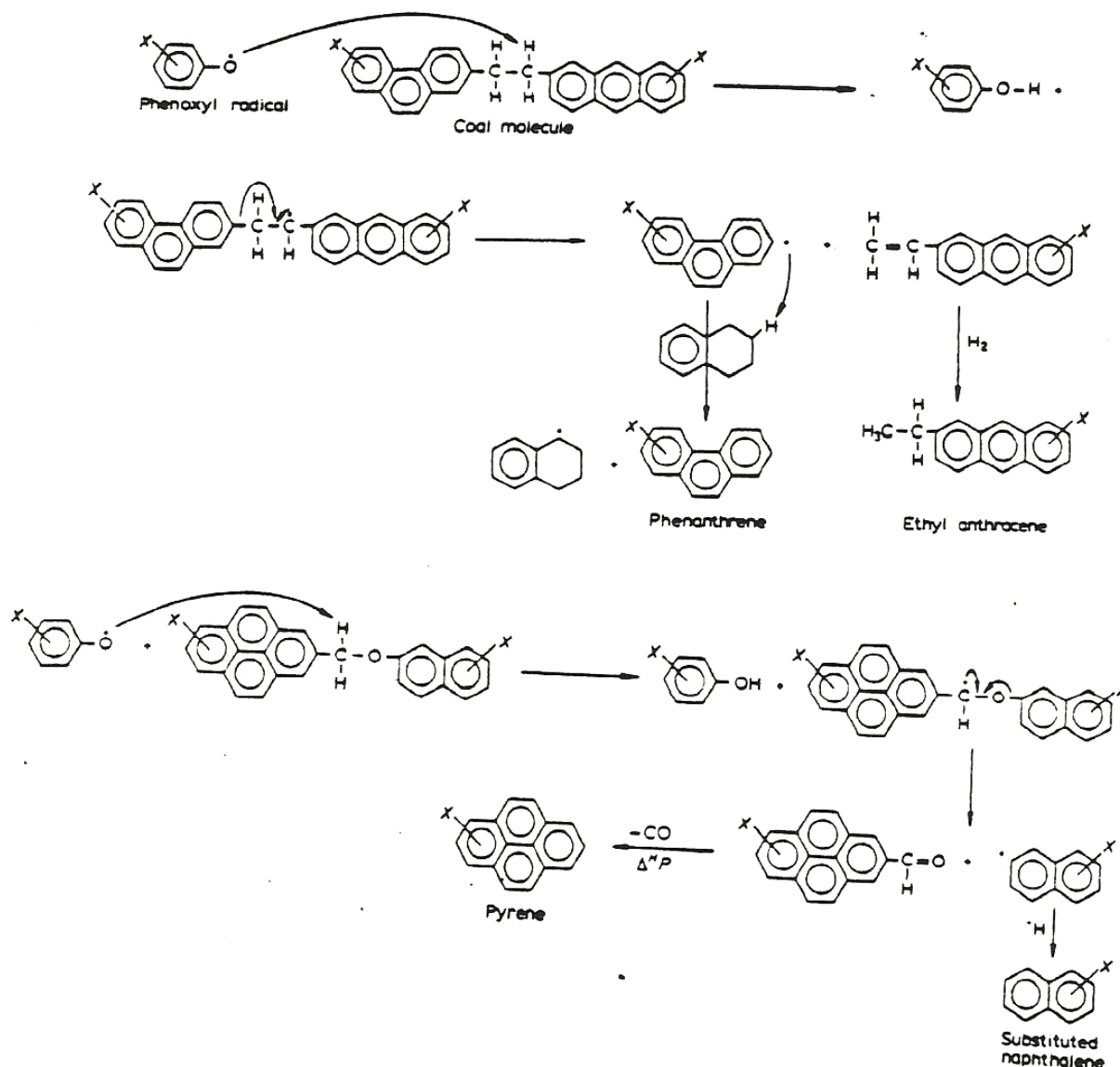


Fig. 8 The reaction mechanisms of phenoxyl radicals with coal

One may ask, could the effects of co-solvent, resulting from liquefaction of the coal and lignin, be responsible for the apparent enhancement in the depolymerization of coal? Proponents of this theory believe that in coal liquefaction systems, the liquids produced during the reaction and solvent used for liquefaction synergistically dissolve the coal. The answer is that co-solvent effects should not be significant due to the high concentrations of tetralin in the system. If the solid-to-solvent ratio was high, then co-solvent effects may become a significant factor; this was certainly not the case in this research.

So far, evidence has been presented which shows that the addition of lignin provides synergistic effects by enhancing the depolymerization of coal. A question that could be asked is: what kind of effects, if any, does coal have on the extent of lignin depolymerization? One way to verify such hypothesis is by producing coal-derived liquids and by reacting them with lignin. The enhancement in lignin conversion due to the presence of coal can then be evaluated.

## 8. Conclusion

This paper outlines the liquefaction processes of coal. They are divided to pyrolysis, solvent extraction, indirect or direct coal liquefaction. Addition of lignin or lignin derived liquids improves the depolymerization of coal. Liquid product quality as measured by molecular weight and aliphatic-to-aromatic hydrogen ratios determined by NMR, was also improved by addition of lignin. More distillable liquid products were obtained from coal-lignin mixtures than those obtained from coal and lignin when reacted separately. Also, the stability of these liquids was better when coal-lignin mixtures were used.

Other hydrocarbon materials should be considered, especially those which are by-products of agricultural industry. As an example olive waste residue can be considered for that purpose [42,43].



## References

- [1] D. Whitehurst, T. Mitchel, M. Fracasiu, *Coal Liquefaction: The Chemistry and Technology of Thermal Process*, Academic Press, New York, 1980.
- [2] B. Akash W. O'Brien. "The production of activated carbon from a bituminous coal". *International Journal of Energy Research*, (1996), 20, 913-922. [http://dx.doi.org/10.1002/\(SICI\)1099-114X\(199610\)20:10<913::AID-ER205>3.0.CO;2-7](http://dx.doi.org/10.1002/(SICI)1099-114X(199610)20:10<913::AID-ER205>3.0.CO;2-7)  
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- [3] N. Berkowitz, *An Introduction to Coal Technology*, Academic Press, New York, 1979.
- [4] J. Newman, "New developments in obtaining chemicals from coal by pyrolysis", in *Chemicals From Coal: New Developments*, K. Payne (Ed.), 1985, Blackwell Sci. Pub., London.
- [5] P. Walker, "Coal derived carbons", *Carbon*, (1986), 24, 379-386. [http://dx.doi.org/10.1016/0008-6223\(86\)90256-3](http://dx.doi.org/10.1016/0008-6223(86)90256-3)
- [6] B. Akash, J. Jaber. "Characterization of shale oil as compared to crude oil and some refined petroleum products". *Energy Sources*, (2003), 25, 1171-1182. <http://dx.doi.org/10.1080/00908310390233612>
- [7] R. Neavel, "Liquefaction of coal in hydrogen-donor and non-donor vehicles", *Fuel*, (1976), 55, 237-242. [http://dx.doi.org/10.1016/0016-2361\(76\)90095-8](http://dx.doi.org/10.1016/0016-2361(76)90095-8)
- [8] D. Fraenkel, V. Pradhan, J. Tierne, I. Wender, "Liquefaction of coal under mild liquefaction conditions", *Fuel*, (1991), 70, 64-73. [http://dx.doi.org/10.1016/0016-2361\(91\)90096-S](http://dx.doi.org/10.1016/0016-2361(91)90096-S)
- [9] R. Skowronski, L. Heredy, "Liquefaction of bituminous coal at moderate temperatures", *Fuel*, (1987), 66, 1642-1645. [http://dx.doi.org/10.1016/0016-2361\(87\)90355-3](http://dx.doi.org/10.1016/0016-2361(87)90355-3)
- [10] M. Mikita, B. Bockrath, H. Davis, S. Friedman, E. Illig, "Water and nondonor-vehicle-assisted liquefaction of Illinois bituminous coal", *Energy and Fuels*, (1988), 2, 534-538. <http://dx.doi.org/10.1021/ef00010a021>
- [11] T. Larsen, T. Sams, B. Rodgers, "Internal rearrangement of hydrogen during heating of coals with phenols", *Fuel*, (1981), 60, 335-341. [http://dx.doi.org/10.1016/0016-2361\(81\)90192-7](http://dx.doi.org/10.1016/0016-2361(81)90192-7)
- [12] K. Chiba, H. Tagaya, N. Saito, "Liquefaction of Yallourn coal by binary system solvent", *Energy and Fuels*, (1987), 1, 338-343. <http://dx.doi.org/10.1021/ef00004a005>
- [13] K. Chiba, H. Tagaya, S. Saito, K. Ito, "Coal liquefaction using indene-tetralin and indene-decalin mixtures as solvent", *Fuel*, (1985), 64, 68-70. [http://dx.doi.org/10.1016/0016-2361\(85\)90280-7](http://dx.doi.org/10.1016/0016-2361(85)90280-7)
- [14] H. Tagaya, K. Katasuma, Y. Shibasaki, K. Chiba, "Coal liquefaction using indene-nondonor mixture as solvent", *Fuel*, (1988), 67, 786-791. [http://dx.doi.org/10.1016/0016-2361\(88\)90151-2](http://dx.doi.org/10.1016/0016-2361(88)90151-2)
- [15] H. Tagaya, K. Takahashi, K. Hashimoto, K. Chiba, "Coal liquefaction by binary solvent systems composed of tetralin and reducible compounds", *Energy and Fuels*, (1989), 3, 345-350. <http://dx.doi.org/10.1021/ef00015a015>
- [16] R. Baldwin, D. Kinner, O. Nguanprasert, R. Miller, "Liquefaction reactivity enhancement of coal by mild alkylation and solvent swelling techniques", *Fuel*, (1991), 70, 429-433. [http://dx.doi.org/10.1016/0016-2361\(91\)90134-V](http://dx.doi.org/10.1016/0016-2361(91)90134-V)
- [17] J. Joseph, "Liquefaction behavior of solvent-swollen coals", *Fuel*, (1991), 70, 139-144. [http://dx.doi.org/10.1016/0016-2361\(91\)90144-Y](http://dx.doi.org/10.1016/0016-2361(91)90144-Y)
- [18] M. Attallah, M. Quezada, M. Wilson, A. Vassalo, "Promotion of coal liquefaction by iodomethane: II. Reaction of coal model compounds with iodomethane at coal liquefaction temperatures". *Energy and Fuels*, (1989), 3, 59-64. <http://dx.doi.org/10.1021/ef00013a010>
- [19] A. Vassalo, M. Wilson, M. Attallah, "Promotion of coal liquefaction by iodomethane: I". *Energy and Fuels*, (1988), 2, 539-547. <http://dx.doi.org/10.1021/ef00010a022>
- [20] S. Yokoyama, M. Yoshida, R. Maekawa, T. Kotanigawa. "Catalytic behavior of sulfate and sulfide in S-promoted iron oxide catalysts for liquefaction of bituminous coal and lignite", *Fuel*, (1991), 70, 163-168. [http://dx.doi.org/10.1016/0016-2361\(91\)90147-3](http://dx.doi.org/10.1016/0016-2361(91)90147-3)
- [21] L. Heredy, A. Kostyo, M. Neuwirth. "Identification of iso-propyl groups on aromatic structure in bituminous coal". *Fuel*, (1963), 42, 182-184.
- [22] K. Ouchi, K. Imuta, Y. Yamashita, "Catalysts for the depolymerization of mature coals". *Fuel*, (1973), 52, 156-157. [http://dx.doi.org/10.1016/0016-2361\(73\)90044-6](http://dx.doi.org/10.1016/0016-2361(73)90044-6)
- [23] H. Hombach, "Particle size and molecular weights of derivatives from coal", *Fuel*, (1982), 61, 215-220. [http://dx.doi.org/10.1016/0016-2361\(82\)90114-4](http://dx.doi.org/10.1016/0016-2361(82)90114-4)

- [24] J. Larsen, D. Lee, "Reaction of coals in hot acidic phenol at constant acid concentration". *Fuel*, (1983), 62, 918-923. [http://dx.doi.org/10.1016/0016-2361\(83\)90161-8](http://dx.doi.org/10.1016/0016-2361(83)90161-8)
- [25] Y. Shen, H. Wu, Z. Pan. Co-liquefaction of coal and polypropylene or polystyrene in hot compressed water at 360–430 °C, *Fuel Processing Technology*, (2012), 104, 281–286, <http://dx.doi.org/10.1016/j.fuproc.2012.05.023>
- [26] Y. Liu, M. Wang, Z. Pan. Catalytic depolymerization of polyethylene terephthalate in hot compressed water, *Journal of Supercritical Fluids*, (2012), 62, 226–231, <http://dx.doi.org/10.1016/j.supflu.2011.11.001>
- [27] Y. Huang, S. Liu, Z. Pan. Effects of plastic additives on depolymerization of polycarbonate in sub-critical water, *Polymer Degradation and Stability*, (2011), 96, 1405–1410, <http://dx.doi.org/10.1016/j.polydegradstab.2011.05.017>
- [28] Shui, H., Shan, C., Cai, Z., Wang, Z., Lei, Z., Ren, S., Pan, C., Li, H. Co-liquefaction behavior of a sub-bituminous coal and sawdust, *Energy* 36 (2011), 6645-6650. <http://dx.doi.org/10.1016/j.energy.2011.08.046>
- [29] F. Karaca, E. Bolat. Coprocessing of a Turkish lignite with a cellulosic waste material: 1. The effect of coprocessing on liquefaction yields at different reaction temperatures, *Fuel Processing Technology*, 64 (2000), 47–55, [http://dx.doi.org/10.1016/S0378-3820\(00\)00076-X](http://dx.doi.org/10.1016/S0378-3820(00)00076-X)
- [30] F. Karaca, E. Bolat. Coprocessing of a Turkish lignite with a cellulosic waste material: 2. The effect of coprocessing on liquefaction yields at different reaction pressures and sawdust/lignite ratios. *Fuel Processing Technology*, (2002), 75, 109–116, [http://dx.doi.org/10.1016/S0378-3820\(01\)00252-1](http://dx.doi.org/10.1016/S0378-3820(01)00252-1)
- [31] H. King, L. Stock, "Aspects of the chemistry of donor solvent coal dissolution: Promotion of the bond cleavage reactions of diphenylalkanes and the related ethers and amines". *Fuel*, (1984), 63, 810-815. [http://dx.doi.org/10.1016/0016-2361\(84\)90072-3](http://dx.doi.org/10.1016/0016-2361(84)90072-3)
- [32] K. Gilbert, J. Gajewski, "Coal liquefaction model studies: Free radical chain decomposition of diphenyl propane, dibenzyl ether and phenyl ether via B-B-Scission reactions". *Journal of Organic Chemistry*, (1982), 47, 4899-4902. <http://dx.doi.org/10.1021/jo00146a016>
- [33] J. Kim, S. Lalvani, B. Akash, C. Muchmore. "Coliquefaction of coal and black liquor to environmentally acceptable liquid fuels". *Energy Sources*, (1999), 21, 839-847. <http://dx.doi.org/10.1080/00908319950014399>
- [34] J. Kim, S. Lalvani, B. Akash. "Coliquefaction of coal and black liquor". *Korean Journal of Chemical Engineering*, (1995), 12, 582-585. <http://dx.doi.org/10.1007/BF02705864>
- [35] C. Muchmore, S. Lalvani, B. Akash. "Coliquefaction of coal and newsprint-derived lignin". *Fuel Processing Technology*, (1994), 37, 203-210. [http://dx.doi.org/10.1016/0378-3820\(94\)90016-7](http://dx.doi.org/10.1016/0378-3820(94)90016-7)
- [36] S. Lalvani, P. Rajagopal, B. Akash, C. Muchmore. "Liquefaction of newsprint and cellulose in tetralin under moderate reaction conditions". *Fuel Processing Technology*, (1993), 35, 219-232. [http://dx.doi.org/10.1016/0378-3820\(93\)90100-I](http://dx.doi.org/10.1016/0378-3820(93)90100-I)
- [37] J. Kim, B. Akash, C. Muchmore, J. Koropchak, S. Lalvani. "Stability of liquids derived from reaction of coal and lignin". *Fuel Processing Technology*, (1993), 33, 175-190. [http://dx.doi.org/10.1016/0378-3820\(93\)90076-G](http://dx.doi.org/10.1016/0378-3820(93)90076-G)
- [38] B. Akash C. Muchmore, J. Koropchak, J. Kim, S. Lalvani. "Investigations of simultaneous coal and lignin liquefaction: kinetic studies". *Energy and Fuels*, (1992), 6, 629-634. <http://dx.doi.org/10.1021/ef00035a014>
- [39] S. Lalvani, P. Rajagopal, J. Koropchak, B. Akash, and C. Muchmore. "Electrolytic pretreatment of coal for enhanced liquefaction". *Fuel Processing Technology*, (1992), 31, 221-232. [http://dx.doi.org/10.1016/0378-3820\(92\)90021-H](http://dx.doi.org/10.1016/0378-3820(92)90021-H)
- [40] S. Lalvani, B. Akash, C. Muchmore, J. Koropchak, C. Chavez, and Rajagopal. "Coal liquefaction in lignin-derived liquids under low severity conditions". *Fuel*, (1991), 70, 1433-1438. [http://dx.doi.org/10.1016/0016-2361\(91\)90010-8](http://dx.doi.org/10.1016/0016-2361(91)90010-8)
- [41] S. Lalvani, B. Akash, C. Muchmore, J. Koropchak, P. Chivate, and C. Chavez. "Lignin-augmented coal liquefaction under mild reaction conditions". *Energy and Fuels*, (1991), 5, 347-352. <http://dx.doi.org/10.1021/ef00026a021>
- [42] T. Al-Khalid, N. Haimour, S. Sayed, B. Akash. "Activation of olive-seed waste residue using CO<sub>2</sub> in a fluidized-bed reactor". *Fuel Processing Technology*, (1998), 57, 55-64. [http://dx.doi.org/10.1016/S0378-3820\(98\)00070-8](http://dx.doi.org/10.1016/S0378-3820(98)00070-8)
- [43] S. Qasem, N. Haimour, S. Sayed, B. Akash. "Salt-catalyzed activation of olive-seed waste residue using a fluidized-bed reactor". *Energy Sources*, (2004), 26, 751-760. <http://dx.doi.org/10.1080/00908310490445580>