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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 byproducts 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 worlds 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 BF₃. 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, nonhomogenous 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 rank.

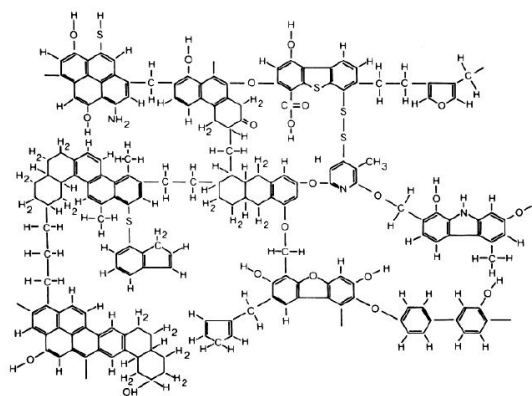


Fig. 1 Bituminous coal Structure

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:

- a) 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.
- b) Combustion: Fluidized bed combustion and advanced slagging combustion. The pollutants are removed as coal is fired.
- c) Post-combustion: Flue gases are cleaned as they exit before they are sent out the smoke stack.

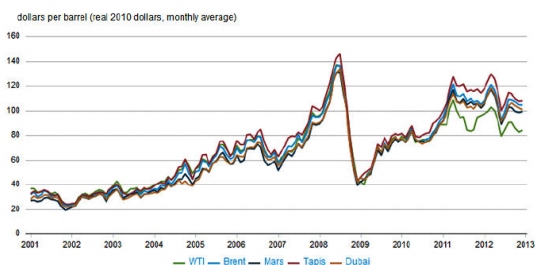


Fig. 2 World crude oil prices for the past 12 years (source: www.eia.gov/finance/markets/images/world_oil_prices.png)

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.

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 nonhydrogen- donor vehicles (e.g., cyclododane) as a suitable liquefaction media. Reactions were carried out in microreactors 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.

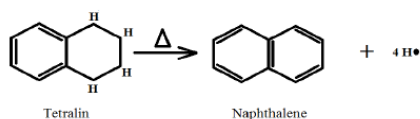


Fig. 3 Chemical reactions showing the donation of four hydrogen atoms for each tetralin molecule

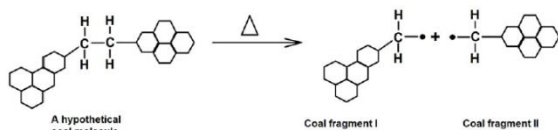


Fig. 4 Chemical reactions showing the formation of free radicals

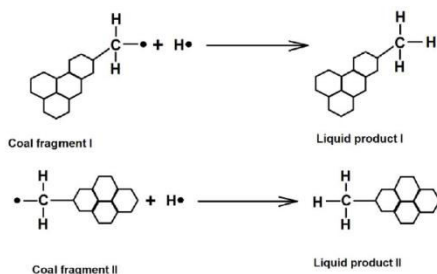


Fig. 5 Chemical reactions showing the stabilization of free radicals by reacting with hydrogen forming smaller molecular weight compounds

6. Coprocessing of Coal with Other Materials

Depolymerization of coal by phenolation was presented. A technique was developed for the depolymerization of coal using BF₃ catalyst in phenol at 100 °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 °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. 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.

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 *I1* and *I2* refer to intermediate products, while *P1*, *P2*, and *P3* refer to final products, whereas, *k1*, *k2*, *k3*, *k4*, and *k5* 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 (*II*) 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 *II* 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 *II*, and hence it should reach a maximum value before it declines.

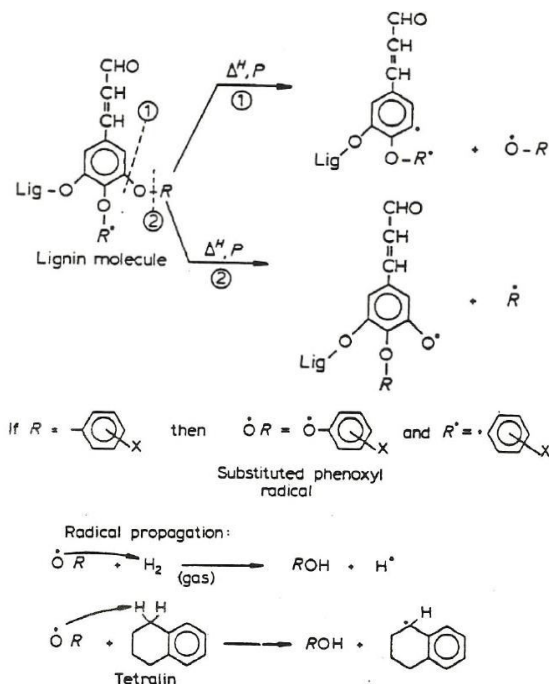


Fig. 7 The formation of phenoxy radical: from thermal hydro-cracking of lignin molecule

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.

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)

[http://dx.doi.org/10.1002/\(SICI\)1099-114X\(199610\)20:10<913::AID-ER205>3.3.CO;2-Z](http://dx.doi.org/10.1002/(SICI)1099-114X(199610)20:10<913::AID-ER205>3.3.CO;2-Z)

[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. Subramanyam Pavuluri <https://orcid.org/0000-0002-2703-2358>

[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. Tiernege, 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 col 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. Shibazaki, 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. Neuworth. “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)