

# ORIGINS AND REACTIONS OF ALKYL AND ALKANES IN DIRECT COAL LIQUEFACTION

ENE C. MORONI

U.S. Department of Energy, FE-25 GTN, Washington, D.C. 20545

## INTRODUCTION

Recent analytical methods have attempted to unveil the nature of the aliphatic part of the molecules present in coal structures, and, with some approximation, they were successful in determining the origins and the size distribution of the alkyl chains and of the linear hydrocarbons. The abundant presence of alkyl groups have been observed among the products of thermal and donor solvent dissolution reactions of various coals. While the analytical determination of alkyls presence in the products of coal conversion and the speculation of their original status in the coal matrix have been extensively studied, their roles in the various reactions occurring in coal liquefaction have not received adequate attention by the research community. In particular, the high severity of operation used in the experimental research works for so many years and, regrettably, even in present research works, has precluded the determination of the role of each of the reactive components existing in the coal structure or formed in various stages of coal liquefaction. In addition, there is a scarcity of information on the role of each of the reactive species and their effect on the reactivity of the other components of coal and coal liquids.

It is commonly accepted that beneficial results are obtained in coal liquefaction by the programmed or staged temperature approach(1), and, currently, this experimental mode has become popular with many researchers.

For a more fundamental approach in coal liquefaction there is an opportunity to study the reactions occurring at the low temperature ranges, say 250-380°C, for each of the reactive components, or each group of components present in coal or formed in the initial stages of liquefaction, which can be related to the most significant beneficial effects observed in the staged temperature experiments.

By increasing the reaction temperature to above 380-400°C, the researcher must be aware that he or she is approaching the threshold separating the predominance of hydrogenation reactions of aromatic compounds at the lower temperatures from those of dehydrogenation of hydroaromatic compounds which occurs at the higher temperatures.

This paper, presently in the form of a communication to be complemented by the oral presentation and expanded for publication in Energy and Fuels, intends to present some of the reactions involving alkyl groups as well as formation of alkanes, which might have important roles in coal liquefaction. The paper has the additional objective to stimulate the research community to undertake a more systematic research approach in liquefaction which ought to separate the many reactions occurring at the lower temperature range from the subsequent reactions occurring at the higher temperatures. The latter are profoundly affected by the way the former are carried out.

## INITIAL STAGES OF COAL LIQUEFACTION

In coal liquefaction experiments, in which coal is slurried in a solvent and heated up to promote coal dissolution, reactions are observed to start at 250-280°C with evolution of mainly CO<sub>2</sub>, particularly evident in low-rank coals. A large conversion of CO<sub>2</sub> to methane has been observed when the reaction off-gas is in the presence of hydrogen pressure and hydrogenation catalysts, and by increasing the reaction temperature from 300° to 380°C. This undesirable reaction consumes hydrogen and creates obvious confusion if one desires to determine accurately the methane derived from the cleavage of methyl groups from the coal structure, at the same or subsequent higher temperatures. Up to date most researchers in coal liquefaction have neglected this occurrence, and, for that matter, to provide full material balances. At the same temperature range in which CO<sub>2</sub> converts to methane, there are other reactions involving the isomerization of alkylphenols. These reactions occur in the presence of gamma-alumina, and perhaps of clays present in the coal mineral matter, such as montmorillonites and illites. By increasing the reaction temperature above 350°C, alkylphenols isomerize to the more thermally stable meta-position. The thermal removal of the hydroxyl groups from meta-alkylphenols is much harder than from the ortho-alkylphenols.

The importance of removing the hydroxyl groups has been emphasized by this author in a previous paper(2), because of the substantial benefits it provides in both liquefaction stage and in the subsequent upgrading stage. An example cited in that paper was the cleavage of the oxygen bridge in diphenyl ether, very often used as model compound reaction related to coal liquefaction according to recent literature, in which the oxygen bridge is cleaved at lower severity if an alkyl group is present in one of the ring, and, in particular, if it is located in ortho-position to the oxygen.

This seems to be in agreement with the fact that oxygen moieties have been removed with ease at much lower severity of experimental conditions in coal liquefaction than from oxygen-containing model compounds commonly used by researchers in this field. This fact would confirm that alkyl groups and, for that matter, other groups which are present in the ring structure of coals, are playing an important role in the initial stages of coal liquefaction. But, given the preponderance of oxygen moieties and the hydrogenation environment required, the predominant feature in coal liquefaction is the dominance of phenolic chemistry.

## SUBSEQUENT LIQUEFACTION STAGES

At higher severity of operations, the phenolic chemistry is still dominant in coal liquefaction, because of the conversion of phenol-precursors to phenols. In the 400-450°C temperature range, transalkylation reactions occur as polyalkylated phenols are able to donate alkyl groups to the non- or less-alkylated phenols, in the presence of clay catalysts(3). At hydrolysis temperature range of 600-1000°C, oxygen in the aromatic rings and hydroxyl groups of phenols were found to strongly enhance the methane yield(4), decarbonylation being the key initial step.

At one point in coal liquefaction perhaps the active oxygen moieties will be practically removed, and other functional groups will probably emerge as

the critical reactive species. However, little is known of the reactions involving alkylated cyclic compounds containing nitrogen and sulfur in the ring. It is believed that the chemistry of alkyl polycyclic aromatics, or hydroaromatics, ought to have a more influential role in the upgrading and refining steps. The selection of the proper catalyst and the experimental conditions in these steps appear to affect the reactions involving alkyl groups, such as, isomerization, transalkylation and "paring" reactions(5).

#### CONCLUSIVE REMARKS

The abundance of various oxygen moieties and alkyl groups in coals, revealed by current sophisticated analytical devices, signifies that they are a critical part of coal reactivity and consequently are having a major effect on the initial stages of coal liquefaction and very likely in the upgrading and refining steps.

Little is known about the homogeneous chemical reactions which, during liquefaction, bring about the reaction of either the removal of each of these groups, or condensation reactions, that is, coupling for the phenols and cyclization for large alkyl groups. Even less known is the effect of one group on the other, and the combined effect on other critical reactions in coal liquefaction.

This communication lists some of the reactions known from unrelated past works which, it is felt, could be profitably pursued in future coal liquefaction research. An amplified version of this communication will be covered during the oral presentation, and a more detailed and complete set of data will be published in Energy and Fuels.

#### REFERENCES

1. Derbyshire, F.J., et al. (1986). Temperature-Staged Catalytic Coal Liquefaction, FUEL, 65, p. 1233, and references cited therein.
2. Moroni, E.C., Coal Liquefaction and Upgrading Benefit from Heteroatom Removal. Proceedings of the 1987 International Conf. on Coal Science, Maastricht, The Netherlands, October 26-30, 1987, p. 351, and references cited therein.
3. Neuworth, M.B., Moroni, E.C., and DelBel, E., Selectivity of Transmethylation of High Boiling Cresylics. U.S. Patent 3,417,149, December 17, 1968.
4. Gobarty, M.L., and Maa, P.S., A Critical Temperature Window for Coal Hydrolysis, Am. Chem. Soc., Div. Fuel Chem. Preprints, 31,(4), 5, 1986, and references cited therein.
5. Sullivan, R.F., et al. A New Reaction That Occurs in Hydrocracking of Certain Aromatic Hydrocarbons. JACS, 83, 1156 (1961).