SECTION IV

COAL LIQUEFACTION WITH

LIQUID CLATHRATES

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Summary

This section provides a review of background information on the application of liquid clathrates for coal liquefaction. The advantages, limitations, and significance of coal liquefaction using liquid clathrates, in particular at low temperatures and pressures, is discussed. Coal liquefaction with liquid clathrates occurs at or near room temperature and requires neither application of heat nor consumption of hydrogen. The unique characteristics of coal dissolution with liquid clathrates lies in that the clathrate acts as a host and does not itself react with the coal. The loss of components used to produce the clathrate is small. However, the yields of coal liquefaction liquids with these clathrates are only about 25 - 40%. The future development of the liquid clathrate technique for coal liquefaction will depend largely on improving liquid yields and finding effective methods for clathrate recovery and regeneration.

Introduction

A liquid clathrate is a group of liquid inclusion compounds which form upon the interaction between a complex salt and an aromatic molecule, whereby the aromatic is entrapped into the complex. Ionic organometallic agents based on $Q_nR_{3n}X$ anions and a range of cations form liquid clathrate phases in aromatic solvents wherein Q is Al, Si or Ga, R is an alkyl group of 1-8 carbon atoms, X is an anion of a mono-, di-, or trinegative salt, and n is an integer of 2 to 4. The liquid clathrate consists of a special ionic compound dissolved in an aromatic solvent (e.g., benzene, toluene) that has the propensity to mobilize and dissolve coal under ambient conditions.

The liquid clathrates have been investigated with regard to their ability to perform separations and as heat transfer media (Atwood, 1977a; Atwood, 1977b). The use of liquid clathrates for separations has been found to provide several unique properties over liquid-liquid extraction. Among these distinct properties are:

1. The guest component in a liquid clathrate consists mainly of an aromatic compound. Although it is possible to force a limited amount of non-aromatic guest into a liquid clathrate, at the final equilibrium state the liquid clathrate contains aromatics almost exclusively.

2. The amount of aromatic loaded in the liquid clathrate phase is fixed and very high; it is immiscible with excess aromatics, i.e., $K[Al_2Me_6N_3]\cdot5.8C_6H_6$ containing 67% by weight of benzene. One could strip out a fraction of the solvent and separated material to leave the remainder to form a "hungry" liquid clathrate for enhancement of separation.

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3. No chemical reaction occurs between the solute and the liquid clathrate; no net stoichiometric consumption of ionic salt components or guest aromatics takes place. The aromatic is trapped by but not bonded to the parent compound.

4. The liquid clathrate structure can be easily broken by a small change in temperature. The dissolved components can be removed from the liquid clathrate by cracking the salt out of the clathrate. The liquid clathrate can be induced to recrystallize at a certain temperature and pressure.

More recently, Atwood (1982) patented a process based on the concept of using liquid clathrates to disperse and dissolve coal at a low temperature and low pressure. Significant amounts of coal organics can be dissolved in the clathrate under ambient pressure and at temperatures between room temperature and the boiling point of the solvent (i.e., benzene, b.p. 80°C). With different ranks of coals, from bituminous to lignite, 20 - 40% net transfer of coal organics to the liquid phase has been achieved by combined dissolution and hydrogenolysis. An effort in this area was funded by Canadian sources (Stobart, et al., 1982) to further investigate potential liquid-clathrate phases for coal liquefaction.

According to Atwood's work (1982), coal is liquefied by admixing the coal with a liquid clathrate. The chemical mechanism for this phenomenon is not fully known, but the essence of the liquid clathrate approach to coal liquefaction lies in the combination of aromatic dissolution with high ionic strength. The high ionic strength of the medium from the liquid clathrate can induce polar fragmentation of the coal structure. The character of the clathrate mobilizes the coal fragments as this ionic attraction is occurring.

The discussion that follows will attempt to review the state-of-the-art of coal liquefaction with liquid clathrates at low temperatures and pressures. Only small amounts of published data on this subject are available and it is not intended here to compare coal liquefaction in liquid clathrates with conventional direct coal liquefaction. The aim, rather, is to understand the formation of liquid clathrates as related to the pathways by which coal fragments form in the clathrate matrix. It is hoped from this review that a more comprehensive picture could be drawn for the future development of this approach.

Liquid Clathrate Formation and Principles

Liquid clathrates consist of aromatic molecules (guests) entrapped within certain geometrical complex salts (hosts) without the existence of a chemical bond between them. In general, a liquid clathrate can be formed when the host compound crystallizes and creates cavities or holes in the lattice that capture the guest compound within the matrix. A strong cation-anion attraction together with a low lattice energy are prerequisites for liquid clathrate behavior. The term "liquid clathrate" was used in 1974 by J. L. Atwood to distinguish a group of compounds which exhibited properties in the liquid state strongly reminiscent of clathrates (Atwood, 1977, Atwood and Atwood, 1976).

In 1960, Ziegler et al. reported the synthesis of compounds of the type $M[Al_2R_6X]$ in Ziegler-Natta catalysis (Cotton and Wilkinson, 1980);

$$MX + 2 \ AlR_3 \rightarrow M[Al_2R_6X] \tag{1}$$

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MX was an alkali metal halide or pseudohalide and R was an alkyl group. In late 1969, Atwood reacted KN_3 with $AlMe_3$ and produced a white crystalline solid, $K[Al_2Me_6N_3]$ (Atwood et al., 1971 and Atwood, 1984),

$$KN_3 + 2 \ AlMe_3 \rightarrow K[Al_2Me_6N_3] \tag{2}$$

observed to be soluble in polar media (e.g., ethers, amines), but not soluble in hydrocarbons. In an attempt to dissolve $K[Al_2Me_6N_3]$ in benzene, he discovered that the material dissolved quickly forming two immiscible liquid layers; an upper layer consisting of pure benzene and a bottom layer consisting of $K[Al_2Me_6N_3] \cdot 5.8C_6H_6$ of liquid clathrate. The liquid clathrates may have the formula

$$M[Q_nR_{3n}X] + \nu \cdot Aromatic \ \underset{\longleftarrow}{\overset{\longrightarrow}{}} \ M[Q_nR_{3n}X] \cdot \nu \ Aromatic \tag{3}$$
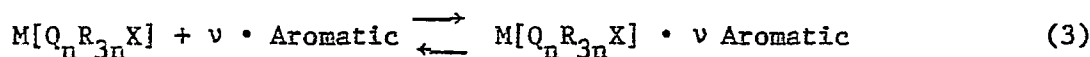
wherein M is a mono-, di- or trivalent cation, R is an alkyl or aryl group, X is an anion of a mono-, di- or trinegative salt, Q is Al, Si or Ga, n is 2-4, and ν is 4 to 40.

Suitable simple salt cations for M include alkali, alkaline earth, quaternary ammonium, phosphonium, arsonium, sulfonium, tellurium or mixtures thereof, including $NR_4^{'+}$, $TlR_2^{'+}$, $PR_4^{'+}$, where R' is hydrogen, a C_1-C_{10} alkyl group, phenyl or naphthyl. The anion X may be any mono-, di- or trinegative anion such as halide, azide, nitrite, nitrate, lower alkyl acyl (e.g., CH_3COO^-, $HCOO^-$), hydroxide, carbonate, sulfate or phosphate. R in the formula may be a lower alkyl of 1-8 carbon atoms, particularly methyl, ethyl, propyl or butyl. When Q is Al, the Al_nR_{3n} component is derived from an aluminum trialkyl compound such as trimethylaluminum, triethylaluminum, or the like.

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The range of components in liquid clathrates of the parent compound, $M[Q_nR_{3n}X]$, is listed in Table IV-1.

It has been demonstrated that benzene and toluene form liquid clathrates (Equation 3). Other aromatic compounds which are suitable in forming these clathrates include xylenes, mesitylene, tetramethylbenzene, dipropylbenzene, diisopropylbenzene, naphthalene, tetralin, anthracene and phenanthracene (Table IV-1).

The ease of formation of the liquid clathrate depends on several factors. The nature of the clathrate interaction is related to the nature of the anion, the lattice energy, the size of the cation and the size of the aromatic molecule. In general, one prefers to have a complex salt having the angular geometry

and a low lattice energy to form liquid clathrates. The formation of liquid clathrates is based to a large extent on the geometry of the anion and the lattice energy. The lattice energy is defined as the energy evolved when the ionic crystal is formed from free ions of infinite distance. For any given structure, the lattice energy is a summation of the coulombic forces of different interionic attraction. In the formation of $K[Al_2Me_6N_3]$ liquid clathrates, the two $AlMe_3$ units greatly restrict the availability of good electrostatic sites for the cations. One may consider the complex of

Table IV-1

Components of Liquid Clathrates, $M[Q_nR_{3n}X] \cdot \nu$ Aromatic Compounds

(Atwood, 1984; Atwood, 1982; Stobart et al., 1982)

M	Q	R	X	Aromatic
Na^+	Al^{3+}	$-CH_3$	F^-	benzene
K^+	Si^{4+}	$-C_2H_5$	Cl^-	toluene
Rb^+	Ga^{3+}	$-C_3H_7$	Br^-	xylene
Cs^+		$-C_4H_9$	I^-	mesitylene
$N(CH_3)_4^+$			H^-	tetramethylbenzene
$N(C_2H_5)_4^+$			N_3^-	dipropylbenzene
$N(C_3H_7)_4^+$			SCN^-	diisopropylbenzene
$N(C_4H_9)_4^+$			$SeCN^-$	naphthalene
$N(C_5H_{11})_4^+$			NO_3^-	tetralin
$N(C_6H_{13})_4^+$			NO_2^-	anthracene
$N(C_7H_{15})_4^+$			$HCOO^-$	phenanthracene
PR_4^+			CH_3COO^-	
$Cr(C_6H_6)_2^+$			O_2^-	
$Co(C_5H_5)_2^+$			OH^-	
$Tl(CH_3)_2^+$			O^{2-}	
Ba^{2+}			SO_4^{2-}	
$K \cdot DB-18-C-6^{+a}$			CO_3^{2-}	
			$C_2O_4^{2-}$	

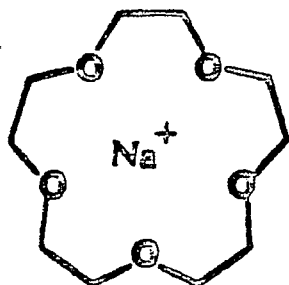a. Potassium $\cdot$ dibenzo-18-crown-6.

$K[Al_2Me_6N_3]$ as lattice energy deficient. The addition of an aromatic solvent affords a stable lattice to allow liquid clathrate behavior.

The formation of liquid clathrates is also strongly dependent on the relative size of the cations and the anions. If the alkyl group, R, of an anion is too large to permit the cation to interact effectively with the negative anion, X, the dimer or trimer of $[M(Q_nR_{3n}X)]$ will be formed simply as a normal solution. For instance, the failure of $K[Al_2Et_6N_3]$ to behave as a liquid clathrate is due to the formation of dimer complex where the bulky ethyl groups isolate the potassium ions from the influence of other ions.

Similarly, if the size of the cation is too small compared to that of the anion, such as $Na[(SiMe_3)_2N]$, a dimer will be formed which can serve to isolate the interaction between the anion and the cation of the parent compound. This will also cause failure of liquid clathrate formation. Clearly, a necessary size ratio of anion to cation is needed to force the ions away from discrete association. Liquid clathrates can, however, be prepared from small cations or anions with large alkyl components by the addition of an apropriate crown ether. Complexation with a crown ether to form a larger cation will form a long-range cooperative interaction between ions in the system so as to avoid the formation of dimer or trimer. For example, by adding dibenzo-18-crown-6 to the normal solution of $K[Al_2Et_6N_3]$ or 15-crown-5 to $Na[(SiMe_3)_2N]$ in benzene, a liquid clathrate immediately results (Figure IV-1).
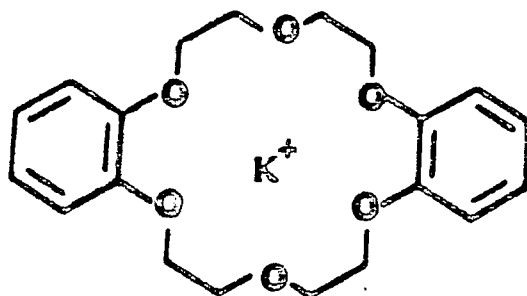
The existence of liquid clathrates based on $[(SiMe_3)_2N]^-$ is important from a practical point of view, because $[Al_2Me_6X]^-$ is sensitive to moisture or oxygen which can attack the aluminum alkyl component and decompose the liquid clathrate. Alternatively, the liquid clathrate based on $M[(SiMe_3)_2X]$ is

(A)

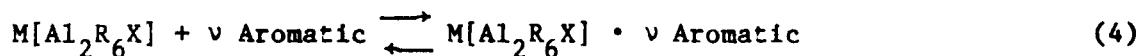Sodium and 15-Crown-5 Complex

(B)

Potassium and Dibenzo-18-Crown-6 Complex

Figure IV-1.   Sodium and Ptassium Ions With Crown Ethers
in Liquid Clathrate Formation.

rather stable to water and oxygen and much easier to work with. In addition, for coal liquefaction, the $AlMe_3$ could alkylate oxygen-containing bonds in coal, but this does not occur with the $-SiMe_3$ unit.

Liquid clathrates have been successfully formed and examined from about a hundred various combinations of different cations and anions with various aromatics (Atwood, 1984). Some examples of liquid clathrates based on the types of parent compound and the aromatic are listed in Table IV-2. The maximum amount of aromatic associated with clathrate ranges from 1 to 42, depending on the sizes of cation, anion and aromatic components in the clathrate. With excess aromatic, two liquid layers (liquid clathrate and pure aromatic) form. With smaller amounts of aromatic, a "hungry" liquid clathrate consumes the solvent up to its maximum amount. The ease of formation of the liquid clathrate is temperature dependent, but once the liquid clathrate has been formed, the maximum aromatic amount is temperature independent up to the decomposition point of the parent complex. The aromatic is trapped by, not bonded to the parent compound, and may be freed by a small change in temperature.

For the parent $M[Al_2R_6X]$ type of liquid clathrate, the following equilibrium pertains.

$$M[Al_2R_6X] + \nu \text{ Aromatic} \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{1cm}{0pt}}} M[Al_2R_6X] \cdot \nu \text{ Aromatic} \qquad (4)$$

The equilibrium lies completely to the left at $20^{\circ}C$ and completely to the right at $30^{\circ}C$. However, the aromatic molecules are necessary constituents of the layer-like liquid structure in the clathrate. They are able to provide additional stabilization by interaction with the parent compounds. A wide range of substances can be attracted in the medium of liquid clathrates, including anthracene, hexane, $(C_6H_6)_2Cr$, and even NaCl to a varying degree.

Table IV-2

Liquid Clathrate Composition Based on Types of Parent Compound and Aromatic Compound
(Atwood, 1984; Atwook, 1982)

Compound	Aromatic	Maximum Ratio Parent Compound/Aromatic
$K[Al_2(CH_3)_6N_3]$	benzene	5.8
$Rb[Al_2(CH_3)_6N_3]$	benzene	6.1
$Cs[Al_2(CH_3)_6N_3]$	benzene	7.4
$K[Al_2(CH_3)_6NO_3]$	benzene	7.0
$Cs[Al_2(CH_3)_6NO_3]$	benzene	12.0
$[N(C_2H_5)_4][Al_2(CH_3)_6NO]$	benzene	9.8
$[N(CH_3)_4][Al_2(CH_3)_6Cl]$	benzene	8.1
$[P(C_5H_5)_4][Al_2(CH_3)_6I]$	benzene	16.1
$[N(C_5H_{11})_4][Al_2(C_3H_7)_6I]$	benzene	42.2
$K[Al_2(CH_3)_6SCN]$	toluene	2.5
$[N(CH_3)_4][Al_2(CH_3)_6F]$	toluene	2.9
$[N(CH_3)_4][Al_2(CH_3)_6Cl]$	toluene	5.6
$[N(CH_3)_4][Al_2(CH_3)_6Br]$	toluene	5.5
$[N(CH_3)_4][Al_2(CH_3)_6I]$	toluene	5.0
$[K \cdot DB\text{-}18\text{-}C\text{-}6][Al_2(CH_3)_6N_3]$[a]	toluene	6.2
$[N(C_2H_5)_4][Al_2(CH_3)_6I]$	ethylbenzene	5.2
$[N(C_3H_7)_4][Al_2(CH_3)_6I]$	ethylbenzene	5.5
$[N(C_6H_{13})_4][Al_2(C_2H_5)_6I]$	o-xylene	39.6
$Cs[Al_2(CH_3)_6N_3]$	p-xylene	2.4
$[N(CH_3)_4][Al_2(CH_3)_6F]$	mesitylene	1.5
$[N(CH_3)_4][Al_2(CH_3)_6F]$	1,2,3,5-tetramethylbenzene	1.3

a. DB-18-C-6 refers to the crown ether dibenzo-18-crown-6.

Use of Liquid Clathrates in Coal Liquefaction

Coal liquefaction with liquid clathrates occurs at or near room temperature and requires neither application of heat nor consumption of hydrogen. The preparation of liquid clathrates has been shown in Atwood's patent (1982). The liquid clathrate can be prepared in one step or in multiple steps. In the one step synthesis, the procedure is simply to add a cation salt and an alkyl anion to an aromatic solvent in the absence of air and water (procedure carried out in a dry box). For instance, mixing 0.05 mol of KN_3 and 0.01 mol of $Al(CH_3)_3$ to ~ 0.1 mol C_6H_6 at $60^{\circ}C$ for one hour affords the liquid clathrate $K[Al_2(CH_3)_6N_3]$ · $5.8C_6H_6$. In multiple steps, the cation salt and the alkyl anion can be mixed and then combined with the aromatic compound.

In the case of coal liquefaction, dried coal about 1 mm in diameter is stirred with a liquid clathrate at a desirable temperature for a certain period of time. After settling, the product extracted from coal is separated by cracking the ionic phase of the liquid clathrate by a change of temperature, followed by centrifugation and filtration. It is claimed that the liquid clathrate turns black instantly upon exposure to coal (Atwood, 1982). The liquid clathrate acts as a solvent and no chemical reaction occurs with coal molecules.

A comparison of coal solvation in different liquid clathrates for various ranks of coals is summarized in Table IV-3. The weight percent of coal dissolved reached 22% depending mainly on temperature, contact time, and coal rank. The data available in Table IV-3 was not sufficient to judge the effect of type of clathrate parent compound. In general, the higher extraction temperature and the longer contact time will dissolve more coal in the liquid clathrate. Coal dissolution in the liquid clathrate is rank dependent. There

Table IV-3

Coal Solvation in Liquid Clathrates
(Atwood, 1982)

Run	1	2	3	4	5	6	7
Sample	Bituminous Coal Mary Lee Seam, AL	Bit. Coal Mary Lee Seam	Bit. Coal Mary Lee Seam	Subbit. Coal Walker Co., AL	Lignite East Central, AL	Tar Sand (North AL)	Bit. Coal Mary Lee Seam
Liquid Clathrate Parent Compounds	$[N(C_3H_7)_4]$ $[Al_2Me_6I]$	$[N(C_3H_7)_4]$ $[Al_2Me_6I]$	$K[Al_2Me_6N_3]$	$[N(C_3H_7)_4]$ $[Al_2Me_6I]$	$[N(C_2H_5)_4]$ $[Al_2Et_6I]$	$[N(C_2H_5)_4]$ $[Al_2Me_6NO_3]$	$(K(18\text{-}Crown\text{-}6))$ $[Al_2Me_6N_3]$
Guest solvent	Toluene	Toluene	Toluene	Toluene	Benzene	Toluene	Toluene
Coal/Liquid Clathrate (gm/ml)	10/100	10/100	10/100	10/100	10/100	10/100	10/100
Temperature, °C	80	Room Temp.	60	60	Room Temp.	Room Temp.	Room Temp.
Contact Time, Hr.	12	48	96	6	4	1	1
Conversion (% Based on Coal Feed)							
Coal Dissolved, %	19	12	22	--	--	---	--
Toluene Soluble, %	4	3	5	6	10	18	3
Toluene Insoluble, %	9	5	9	--	--	--	--

is a trend of increasing toluene-soluble product with lower rank coals, e.g., 3-5% forbituminous coal, 6% for subbituminous and 10% for lignite, respectively. The high contents of oxygen-containing polar components in low rank coals might play an important role during coal liquefaction in liquid clathrates.

The oil product (toluene-solubles) from coal liquefaction with liquid clathrate has an average molecular weight from 40 to 300 and a boiling point from 30 to 250°C. Under low-temperature operating conditions (25 - 80°C), it was observed that hydrogen is retained in the products, as coal goes from the solid phase into the liquid phase without loss of volatile compounds. In most cases, the liquefaction of coal in liquid clathrate occurs at or near room temperature.

Although the precise mechanism of coal liquefaction in liquid clathrates is far from being fully understood, a conjecture would be that the high ionic strength of the liquid clathrate medium induces polar fragmentation in the coal structure and forms a complex held together by the coal-clathrate phase. Recent reports (Sandia Report, 1984; Larsen, 1985) support the view that strong hydrogen bonds exist in coal, particularly in Illinois #6 and low-rank coals. The character of the clathrate would mobilize the coal polar fragments as the coal hydrogen bonds are disrupting.

The liquid clathrates have another unique property: they dissolve substances which act as homogeneous catalysts. Atwood (1984) demonstrated the incorporation of hydrogenation catalysts such as $(C_6H_6)Cr(CO)_3$ or $(C_5H_5)Mn(CO)_3$ in the liquid clathrate $[NEt_4][Al_2Me_6I]\cdot6.4$ toluene with H_2 gas bubbling through the phase. A significant increase in coal dissolution in liquid clathrate was found with a catalyst; for instance, the amount of coal dissolved increased to 40%. Incorporation of hydrogen in the volatile

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products has also been observed although exact numbers were not determined (Stobart, et al., 1982).

It is believed that the mechanism of catalytic hydrogenation of coal dissolution in liquid clathrates involves coal reactive fragments derived immediately after dissolution being hydrogenated with an immobilized homogeneous catalyst. Meanwhile, saturated hydrocarbons are preferentially transferred from the clathrate into the solvent; then, subsequent equilibrium would extract a further amount of aromatic type of material from the coal into the clathrate resulting in higher yields and better product qualities. Catalysts such as arene-transition metal complex cations which are compatible with the liquid clathrate and are ionic in character are suitable to serve as hydrogenation catalysts in the clathrate phase. Potential candidates for hydrogenation catalysts in liquid clathrates are listed in Table IV-4. Although their full catalytic potential has not yet been well established, some have already been tested (Stobart, et al., 1982).

Several limitations or restrictions associated with coal dissolution in liquid clathrates must be overcome before a continuous phase or a large-scale operation can be considered. Some of these are listed below:

(1) The overall yield of coal dissolution in the liquid clathrate is about 20 to 40%. This seems close to, but not better than, the limit of coal extracted or dissolved in most good coal solvents. The amount of coal dissolved seems to be controlled by the breakage of hydrogen bonds or of oxygen-containing groups such as ethers, hydroxyl groups, carboxylic groups, or phenols in the coal structure.

(2) The aluminum alkyls used in the liquid clathrate are thermally unstable at high temperatures. Beyond 190°C, the aluminum alkyl will decompose. In

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Table IV-4

Potential Catalysts for Hydrogenation in Liquid Clathrate Phases

(Stobart et al., 1982)

Type of Catalyst   Remarks

● Arene-transition-metal complex cations

$ArFeCp^+$ $Ar = C_6H_6^-$

$Cp = C_5H_5^-$

$FeCp_2^+$

Ar_2Cr^+

● Arene-carbonyl (Cr, W, Mo) complex cations

$ArMoCo^+$

● Rhodium- or iridium-phosphine complex cations

● Tetracarbonylcobalt anions

$Co(CO)_4^-$

● Hydridocobalt complex anions

addition, the clathrates discussed here are moisture and oxygen- -sensitive. Moisture or oxygen will attack the aluminum alkyl component of the salt, although the reactivity of the parent compounds in the liquid clathrate is, in general, much less than that of the aluminum alkyls themselves.

(3) The particle size of coal will affect the period of contact time needed with the liquid clathrate. Agitation or stirring must to be applied during the contact time to reduce diffusion limitations. Fine coal particles with large surface areas enable maximum contact with the liquid clathrate.

(4) The liquid clathrate phase, by continued operation, could accumulate materials which cannot be regenerated due to the various ionic components on the coal surface. The liquid clathrate will gradually saturate its solvating power. The primary requirements for the components consisting of the liquid clathrate must be low cost, easy regeneration, and hydrolytic stability.

Conclusions and Recommendations

Direct coal liquefaction requires considerable energy input to liquefy coal at high temperatures (350 ⁻ 500°C) and high pressures (above 2000 psi). Under these comparatively severe conditions, large amounts of hydrogen are consumed and/or are lost as the coal goes from the solid phase into liquid or gaseous phases. Coal liquefaction in liquid clathrates provides a low-temperature approach to dissolve coal in the range of 25 - 100°C that is far below the temperatures of ordinary direct coal liquefaction. The unique characteristics of coal dissolution with liquid clathrates include:

(a) coal liquefaction occurs at or near room temperature requiring neither application of heat nor consumption of hydrogen;

(b) a substantial quantity of coal can exist in a liquid clathrate, up to 25% when employing low rank coals;

(c) addition of ambient H_2 to the liquid clathrate in the presence of a homogeneous hydrogenation catalyst leads to an increase of dissolved coal (up to 40%) with a higher hydrogen content;

(d) the liquid clathrate acts as a host and does not itself react with coal molecules; the loss of components used to produce the clathrates is small;

However, many basic questions as to coal liquefaction in liquid clathrates can be posed. Some are:

(1) Is the mechanism of the dissolution of coal in liquid clathrates physical in nature, as most investigators claim? Or is the coal being chemically modified in some manner; in particular do surface reactions occur?

(2) What parts of the coal undergo preferential dissolution in the clathrate? Is any particular maceral more reactive (soluble)?

(3) There is a rank dependence in the dissolution of coal in the clathrate. Does this indicate that the degree of coal dissolution is affected by oxygen-containing groups or by minerals, or by both? What is the function of inorganic salts or minerals in the coal dissolution?

(4) How does addition of a homogeneous catalyst with bubbling H_2 increase the amount of coal dissolution and enhance the hydrogen content of the product?

(5) How does the high molecular weight residue separate from the clathrate phase? How much of the liquid clathrate is lost to the residual coal? Which types of mineral matter are accumulated in the clathrate phase?

(6) What types of effects do clay minerals or other ionic configurations on the coal surface impose?

There are many areas that need further study in order to assess this approach of coal liquefaction with liquid clathrates. Probably, the most important research priority is to understand the mechanism by which coal components dissolve in the liquid clathrate. Understanding the mechanism involved in coal dissolution with the liquid clathrate might lead to a low-temperature, perhaps cheap, coal liquefaction process and a better understanding of the constitution of coal structure. The following research areas are recommended for further investigation to improve product yields and possibly to eventually reduce process costs:

● The effectiveness of premodification of the molecular structure of coal to increase ionic concentrations so as to improve coal dissolution in liquid clathrates should be investigated. Sternberg et al. (1971) have successfully treated coal with alkali metals to transfer negative charges to the aromatic clusters in the coal. It might be possible first to introduce aromatic hydrocarbons anions into the coal macromolecule and

then allow these anions to dissolve in the liquid clathrates. This might improve the amounts extracted by the clathrates so that they exceed the amounts of coal dissolved in most solvents. Recently, Larsen (1985) proposed a coal model with large numbers of active hydrogen-bonded cross-links in the coal cluster, indicating the importance of electrostatic features in the coal macromolecules.

- One of the potential research areas would be to activate coal clay minerals or other ionic configurations in coal so as to interact or replace cation components in the liquid clathrate with subsequent enhancement of coal dissolution. Clathrate-like compounds can be formed by stirring coal with iron(III) chloride (Kochkanyan et al., 1985) where $FeCl_3$ could penetrate into the newly-expanded pores of the coal structure and form a donor-acceptor type coal-$FeCl_3$ association.

- Homogeneous catalysts enhance the coal dissolution and upgrade the coal products in the clathrate phase. Potential catalysts (as listed in Table IV-4) should to be further explored to ensure better contact among catalyst, coal, hydrogen, and the liquid clathrate. Complex organometallic ions such as Co, Mo, Ni, Fe, Rh, and Ir arene-carbonyls are of particular interest. The efficient utilization of hydrogen either by bubbling H_2 gas through the phase or by applying elevated pressure is also important during the homogeneous hydrogenation catalysis of coal liquefaction in liquid clathrates. Adding CO, which may be more reactive with low-rank coals, might improve coal dissolution.

- Liquid clathrate parent components based on the aluminum alkyl anion, $[Al_2Me_6N_3]^-$ are thermally unstable and also react with oxygen, air and water. Development of new ligand systems that are low cost and more stable, such as the silicon-based anion, $[Si_2Me_6N]^-$ appears to be an

important way to go. The silicon-based compounds are much easier to work with than those of aluminum. Liquid clathrates can be prepared from Li[N(SiMe$_3$)$_2$] or Na[N(SiMe$_3$)$_2$] by the addition of an appropriate crown ether.

● The effectiveness of the clathrate technique for coal liquefaction also lies in the development of effective methods for clathrate recovery and regeneration. The extraction system must be investigated thoroughly in order to learn how to efficiently strip the liquid clathrate from the enriched products. The regeneration of liquid clathrates can be studied either by changing the solvent or by changing the temperature sharply to break the ionic phase and crack the salts or contaminants out of the clathrate.

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