

A PHOTOMICROGRAPHIC STUDY OF COAL DISSOLUTION

by

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A critical step in several of the processes for production of liquids from coal is the dissolution of coal in a suitable carrier solvent. An example is the noncatalytic solvent refining of coal(SRC) process in which coal is slurried with a solvent and, in the presence of hydrogen gas, heated to 375 - 425°C. Subsequent filtration of the resulting solution and distillation of the solvent leaves a solid (solvent refined coal) low in ash and sulfur, suitable for use as a boiler fuel. The actual dissolution appears to involve both chemical and thermal phenomena, and although it has been shown to be technically feasible, the exact mechanisms and the rate-limiting steps have not been defined clearly.

The highly porous structure of coal suggests that intraparticle mass transfer and diffusion could play a vital role in its dissolution. Likewise, fluid-particle transport phenomena cannot be ruled negligible *a-priori*. If these effects are appreciable, then the size of the coal particles should be an important operational variable; for, the larger the size of the particles, the longer the diffusional path and the smaller the ratio of external to internal surface area. Typically, however, as reported by Curran *et. al.*¹ and others², the rate of dissolution has been observed to be independent of particle size. A few studies^{3,4}, on the other hand, show particle size to be a variable of some importance. Additional investigations in this area thus seem warranted.

Hill, *et. al.*⁵ have applied Eyring Absolute Reaction Rate Theory to the kinetics of the dissolution of bituminous coal in tetralin. Average heats of activation and apparent entropies of activation are presented, and marked changes are shown to occur in the entropy of activation as dissolution proceeds. This is interpreted to imply that the fraction of reaction sites available for reaction increases drastically during dissolution. The exact manner and rate of particle break-up to form these additional reaction sites, however, has not been clearly established.

Dryden⁶, proposed that dissolution occurs by the removal of units of colloidal size directly from the coal. He maintains that coal consists of a matrix of larger, strongly linked micelles which are intimately associated with smaller, less strongly bonded micelles and that dissolution occurs by removal of these colloidal units, with the smaller micelles dissolving and the larger ones being indestructible at the temperature of dissolution. He explains further that the difference between these two micelles is one of degree rather than kind in that they probably form a continuous series with the dividing line being determined by the temperature. A model similar to Dryden's is given by Hill⁵, *et. al.* with the exception that they consider the idea of an indestructible micelle to be untenable in light of their observation that activation energy increases continuously with dissolution.

Another proposed description for the dissolution of coal, which is completely opposite in concept to Dryden's model, is reflected in A. Gillet's⁷ analysis of dissolution at high temperatures (360°C) in hydrocarbon solvents such as anthracene oil and phenanthrene. He hypothesizes that coal dissolves as a unitary substance - like gelatin in water - to form unstable compounds (or complexes) which gradually decompose and that, even when the temperature is maintained constant, a considerable part of the dissolved material is precipitated within a comparatively short time. Lowry⁸ appears to have confirmed this hypothesis by observing solutions of coal in tetralin at 300°C to be optically clear when hot, but to become rapidly colloidal when allowed to stand.

Ashbury³, in his study of benzene pressure extraction of Edenborn coal, also observed precipitation of extract to occur with cooling. Yet, he differed from Gillet's hypothesis by inferring that the extract would remain as a true solution if the temperature were held constant, for his precipitated material redissolved when heated only to 80°C. Assuming that coal extracts are true solutions, Curran¹ et.al. derived a reaction model capable of representing well experimental data for coal dissolution in active hydrogen-donor solvents such as tetralin. Moreover, they state that no evidence exists supporting the formation of colloidal mixtures since the coal extract solutions could be filtered without deposition of extract through a filter with a pore size of only 100 Å.

In light of the above investigations, it appears that some controversy exists regarding the exact mechanism of particle-liquid interaction in the dissolution process. Generally, however, it appears from these earlier studies that particle size is of more importance in the low temperature solvent extraction of coal as opposed to the more complete dissolution obtained using high temperature hydrogen donor solvents. Thus, while it may be surmised that individual coal particles retain their integrity longer in the former processes, quantitative data on this facet of dissolution at high temperatures is lacking. The purpose of this study is to elucidate the mechanism by which individual coal particles dissolve at high temperatures and, thereby, to attempt to resolve and extend some of the observations of earlier investigators. In this belief that visual evidence would be enlightening, this study was based on monitoring the change in particle size at various stages in the coal dissolution process utilizing a previously somewhat neglected technique - that of photomicroscopy. From the evidence obtained in this manner, some conclusions may be drawn regarding the importance of fluid-solid phenomena in coal dissolution, and the applicability of homogenous phase reaction kinetics. In addition, some new insights into the relative roles of gaseous hydrogen versus donor solvent hydrogen are offered.

Experimental

Kentucky No. 9 coal was crushed and sized by screening for use in the experiments. The analysis of the original coal and that of each fraction after screening is shown in Table 1, where the composition of each size fraction is seen to be similar. The -60 +80 fraction was selected for use in the experiments. The solvents used were creosote oil (Table 2) (start-up solvent for the SRC plant at Wilsonville, Alabama), paraffin oil (Will Scientific Co.), decalin, and tetralin (Eastman Kodak). Hydrogen and nitrogen gases were the 6000 psi grade supplied by Linde. A 6/1 solvent to coal weight ratio was used in all experiments reported here. All coal was dried overnight at 100°C and 25 inches Hg vacuum before use.

An Autoclave Engineers' 300 cc magnedrive autoclave was used as a reactor, with auxiliary equipment for slurry injection and for liquid sampling. The autoclave was equipped with a turbine agitator, baffle, cooling coil, thermowell, and five ports. These ports were used for: (1) rupture disk, (2) slurry injection, (3) gas inlet, (4) liquid sampling, and (5) gas sampling. The autoclave was heated by an electric furnace surrounding the base and controlled by means of a powerstat or automatic controller. Chromel-alumel thermocouples and a Bristol multi-point recorder were used to indicate temperature.

The autoclave was equipped with a cylinder and piston arrangement designed for quick sample injection into solvent preheated to reaction temperature. This injection procedure was used in preliminary experiments with the somewhat surprising result that, at 400°C, all coal particles dissolved before a sample could be withdrawn from the reactor, a time period of about one minute. To alleviate this situation, the injection procedure was replaced by one in which batches of coal and solvent were heated together to a sequence of increasingly higher temperatures. Upon reaching the desired temperature for a particular experiment, the resulting mixture was immediately quenched to room temperature, a Soxhlet extraction with acetone was performed and a photomicrograph at 50X was made of the residue remaining in the Soxhlet thimble.

To insure that only individual coal particles were photographed, the residue was treated in an ultrasonic bath to disperse all agglomerates. The slide mounting medium used was Araclor 5442, a thermoplastic resin produced by Monsanto. Several drops of Araclor, heated to above its melting point was dropped onto a slide, smeared out, and allowed to become tacky. A drop of the residue dispersed in acetone was then dropped onto the Araclor on the slide which then was placed on a hot plate until the Araclor remelted. Finally, the particles were dispersed in the Araclor by stirring with a toothpick, the dispersion covered with a cover-glass, and allowed to cool and harden. The slide was examined under the microscope for areas of good dispersion and photographs were made of those areas. A Leitz Panphot Photomicrograph equipped with a Polaroid 4x5 film holder was used for particle size comparison. Further details concerning the above procedures are given by Green⁹.

Results and Discussion

Experiments were conducted to explore the roles of temperature, hydrogen donor activity, and gas phase composition upon the dissolution of coal. All three variables were found to have significant effects. The results from this work do not establish whether coal dissolves forming a true solution and partially re-precipitates during analysis or whether it simply fragments into smaller units during the initial stages of dissolution. It is likely that a combination of these two mechanisms actually takes place. For this reason, the term disintegration is introduced to represent the overall process by which the smaller particles are formed.

Effect of Temperature

From Figures 1a - f, it is obvious that temperature plays a highly significant role in the dissolution process. No apparent disintegration of the coal particles occurs until a temperature of 340°C is reached, at which time fragmentation begins. At 350°C considerable disintegration has taken place and no original coal particles remain intact. At 360°C disintegration appears complete and, in fact, additional reaction at 400°C for two hours produces no further changes in physical appearance as shown in Figure 1f.

These results appear to explain the marked changes in apparent entropy of activation observed by Hill⁵, which can be attributed to a sudden increase in available reaction sites. Such an increase is in line with the speed of coal disintegration observed here. The fact that particle disintegration occurs almost instantly once a temperature of about 350°C is reached also shows why injection type experiments, in which samples could be collected at a minimum of two minute intervals, were unsuccessful for monitoring the extent of particle break-up. Heat transfer calculations¹⁰ give the time required for a 0.2 mm diameter coal particle to reach the solvent temperature after injection as only

about 0.2 sec and hence the disintegration occurs so rapidly, once a high enough temperature is reached, it is reasonable to conjecture that the thermally activated reaction is controlled by the heat transfer rate to the particle, which is very fast for the small particles used here. As seen from Figure 1, a high activation energy is required for disintegration, as implied by the drastic changes occurring with the relatively small changes in temperature from 330 to 340°C and from 340 to 350°C.

It is very interesting to note that in each of the experiments represented in Figure 1, the amount of acetone solubles as determined by Soxhlet extraction remained very low (less than 10 per cent) despite the drastic changes in particle size. Figure 2 indicates how the yield based on acetone solubles changes with reaction time, with the yield of 50 per cent at two hours corresponding to the photomicrograph given in Figure 1F. Thus, we can conclude that the yield measured by Soxhlet extraction tests is not directly related to the early dissolution of the solid coal particles. At these early stages, it appears that a significant fraction of the coal already dissolved re-precipitates during the Soxhlet extraction. This is supported by the fact that the acetone insoluble residue remains at the same size despite the length of reaction time. Further evidence is provided by the photomicrographs given in Figure 3, obtained using a scanning electron microscope. The particles appear to be of uniform size and have a globular appearance as would be expected with re-precipitated material. The large particles in Figure 3 are assumed to be mineral matter, this is presently being verified.

These observations and implications raise some question as to the significance of obtaining reaction kinetics using acetone insolubles (or as more commonly reported, benzene insolubles). If a true solution is formed once a sufficiently high temperature is reached, as proposed by Gillet⁷ and inferred above, benzene insolubles, as currently determined, probably do not represent conditions existing at the reaction temperature and pressure. The relationship between insolubles and actual dissolution is thus somewhat obscure. Yet, this measure is often used as the characteristic parameter in treating the kinetics of dissolution and is typically assumed to correlate well with the degree of depolymerization of the coal. Since additional reactions and considerable precipitation of coal extract may occur while determining Soxhlet insolubles, some doubt may arise as to the meaning of a kinetic treatment of dissolution based on benzene insolubles, and this matter should be the subject of further investigation. In any event, it does appear that a distinction must be made between the amount of MAF coal undissolved at reaction conditions and the amount of insolubles as determined by Soxhlet extraction.

Effect of Hydrogen Donor Activity

While the above sequence has shown dissolution to be a thermally activated process, these further experiments show that application of heat alone is insufficient to disintegrate the coal particles in the temperature range used here. Rather, these photomicrographs show that hydrogen transfer is a necessary prerequisite for disintegration.

The effect of four different solvents having varying hydrogen donor capacities is shown in Figures 4a-e. All four reactions were conducted for two hours at 400°C in their respective solvents. Tetralin and creosote oil, the best hydrogen donors, disintegrate the coal effectively, while paraffin oil, which donates little hydrogen, has virtually no effect on the coal. Decalin is an intermediate strength hydrogen donor. Curran¹ et. al. for instance, report only 0.28 per cent hydrogen transfer to MAF coal using decalin as opposed

to 1.21 per cent with tetralin. From Figure 4c it is observed that the coal only partially disintegrates in decalin. Thus, a direct correlation exists between coal disintegration and hydrogen donor activity of the solvent.

From the results in paraffin oil, it is obvious that the application of heat alone at 400°C is insufficient to disintegrate the coal particles, while disintegration occurs readily at that same temperature with a solvent capable of providing sufficient hydrogen, as exemplified by the tetralin and anthracene oil results. Apparently then, disintegration occurs as a fast fluid-solid hydrogenation surface reaction having a high activation energy. In processes such as the solvent refining of coal, therefore, the liquefaction stage should be treated as a chemical process rather than as a strictly thermal process as in pyrolysis.

Effect of Gas Phase Composition

Often in coal liquefaction operations supplemental gaseous hydrogen is added to the solvent-coal slurry; however, little information is available as to the relation between hydrogen transfer from a donor solvent versus that from gaseous hydrogen. The experimental results of Figure 5 clearly show that hydrogen may be donated directly to coal particles in the absence of a donor solvent and that this will result in particle disintegration, although at a somewhat slower rate than when a donor solvent is present. Here, the rate of disintegration may be limited by intraparticle diffusion of dissolved hydrogen gas in the liquid filled pores. Such diffusion would be unnecessary were the pores filled with a solvent capable of donating hydrogen directly. The necessity for providing some form of hydrogen for particle disintegration is apparent from the negative results in Figure 4d, obtained using a nitrogen atmosphere with paraffin oil as a solvent.

Conclusions

From this photomicrographic study, it can be concluded that the disintegration of coal particles in a hydrogen donor solvent occurs almost instantaneously at 360°C, although the application of heat alone is insufficient to render the particles soluble at this temperature. The necessary hydrogen for disintegration may be provided also by molecular hydrogen as a dissolved gas, although perhaps at a slightly slower rate than from a donor solvent. The rapidity of particle disintegration suggests that heat transfer to the particle may be rate controlling, although this would be unimportant from a practical processing standpoint. It appears that a direct relationship between particle dissolution and insolubles from Soxhlet extractions is difficult to ascertain, because of the possibility of reprecipitation of dissolved coal species. These results also indicate that hydrogenation and hydrodesulfurization take place on a much longer time scale than particle disintegration and that these two processes may be regarded as occurring in a homogeneous liquid phase, rather than as a fluid-solid surface reaction of the type present in hydrogasification. The speed with which particle disintegration occurs partly explains the lack of importance placed upon initial particle size and agitation rate in non-catalytic coal liquefaction processes.

Acknowledgement

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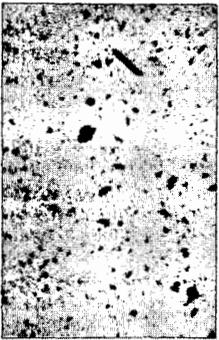
(a) original coal



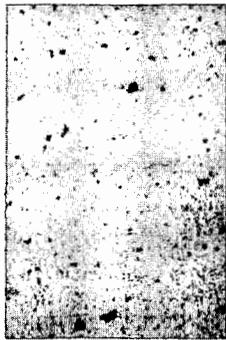
(b) 330°C



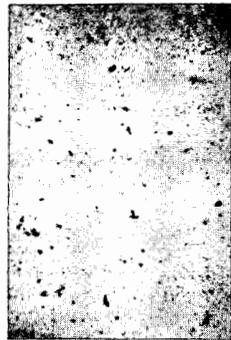
(c) 340°C



(d) 350°C

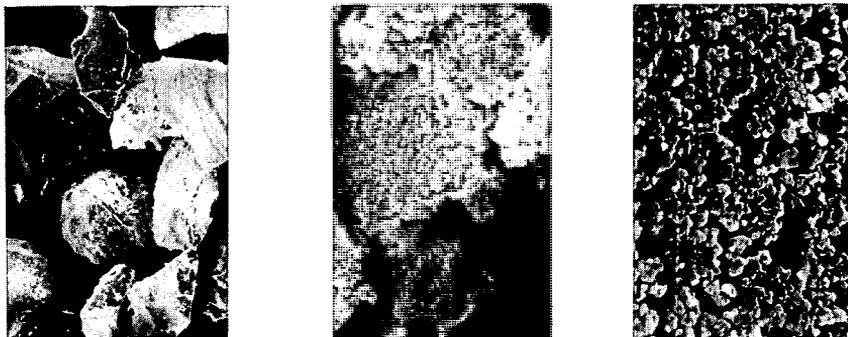


(e) 360°C



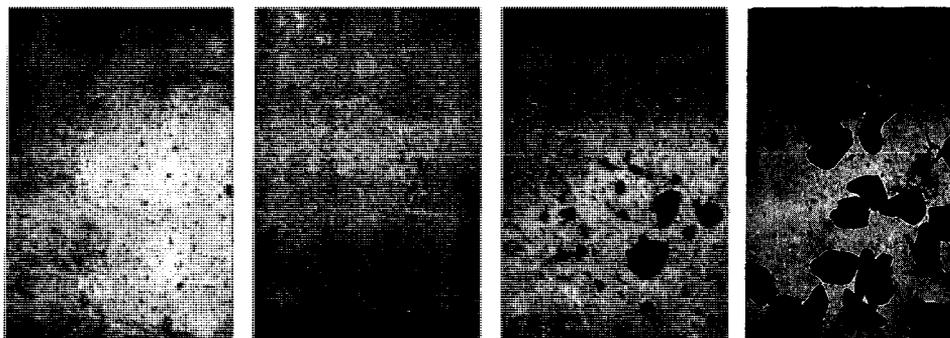
(f) 400°C, 2 hours

Figure 1: Effect of temperature on the disintegration of -60 +80 mesh coal particles using creosote oil and hydrogen atmosphere



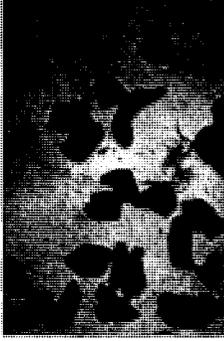
(a) original coal particles, 100x (b) Soxhlet residue, 500x (c) Soxhlet residue, 1000x

Figure 3: Residue from Soxhlet Acetone Extraction after dissolution
in creosote oil and hydrogen gas at 360°C

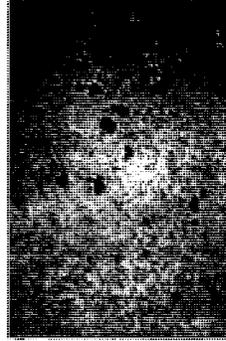


(a) creosote oil (b) tetralin (c) decalin (d) paraffin oil

Figure 4: Effect of solvent hydrogen donor activity on particle
disintegration after 2 hours at 400°C with nitrogen
atmosphere



(a) nitrogen atmosphere



(b) hydrogen atmosphere

Figure 5: Effect of gas phase composition on particle disintegration
at 400°C after 2 hours in paraffin oil

TABLE 1

ANALYSIS OF KENTUCKY NO. 9 COAL AND SIZE FRACTIONS

FRACTION	ASH Moisture Free %	Carbon %	ULTIMATE Hydrogen %	ANALYSIS(MAF) Nitrogen %	Sulfur %
Original	10.2	77.8	6.4	1.5	3.8
-25 +35	9.8	77.4	6.6	1.5	4.2
-35 +45	9.6	77.4	6.4	1.4	3.8
-45 +60	8.8	78.0	6.8	1.3	3.8
-60 +80	9.0	76.0	5.6	1.2	3.8
-80 +120	8.5	73.5	5.7	1.2	3.7
-120 +170	8.4	74.4	5.4	1.2	3.6
-170 +230	7.3	76.1	6.3	1.5	3.8
-230 +325	9.1	85.6	5.8	1.6	4.2
-325 +400	9.5	86.8	5.9	1.6	4.0
-400	10.6	74.3	5.4	1.4	4.5

Table 2

MAJOR COMPONENTS IN CREOSOTE OIL

Naphthalene	10%
2-Methylnaphthalene	8%
1-Methylnaphthalene	3%
1,2-Dimethylnaphthalene	9%
Acenaphthalene	5%
Fluorene	5%
Anthracene and Phenanthrene	17%
Carbazole, Fluoranthene, Pyrene	5%
Other (about 30 identified)	<u>38%</u>
TOTAL	100%

Figure 2
Dissolution Rate Curve for Injection Run
(400°C, 6:1 Creosote Oil to Coal Ratio, 1500 rpm agitation, and 1,000 psig H₂)

