EXPERIMENTAL ANALYSIS OF DIRECT COAL LIQUEFACTION
BY AN AUTOCLAVE EQUIPPED WITH SAMPLING CELLS

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Key Words: Coal Liquefaction, Chemical Reactor, Sampling, Mass Transfer, Vehicle Effect, Energy

To solve some problems of conventional experimental analyses of coal liquefaction, other workers have proposed a method utilizing an autoclave equipped with sampling cells with which reacting coal pastes can be sampled as such. They have not showed how to apply the method accurately, however, nor its effectiveness in comparison with conventional analyses. In this work an accurate procedure for applying the method was developed and efficiency was demonstrated. Some of the experimental findings by application of the procedure developed were as follows: (1) the real product distribution under liquefaction conditions was obtainable, while the conventional analyses gave only an apparent product distribution under ambient conditions; (2) the coal slurry holdup was reduced because of considerable conversion of the slurry into gaseous products with the progress of liquefaction.

Introduction

Coal liquefaction has been experimentally analyzed with various types of batch reactors, such as a shaking autoclave. Analysis of the reaction with such conventional reactors involves some problems, however. First, the experimental procedure consumes much times, because of the necessity of several batches for even one isothermal reaction course. Also, the course observed is apparently isothermal owing to the effects of reaction progress during the periods for heating up and cooling down the reactors, and therefore the rate analysis is rather tedious. Finally, the product distribution obtained may be only an apparent one, because it is determined after cooling the reactors and hence gaseous compounds condense and are analyzed along with liquid products.

To solve these problems some countermeasures have been proposed, but they cannot be effective against the last problem noted above. Thus, a method in which reacting mixtures can be sampled as such has been developed as an alternative. The previous reports, however, did not discuss in detail its accurate application or its effectiveness.

In the present work an experimental procedure was developed to apply the method accurately and its effectiveness compared with conventional methods was shown. Application of this procedure was found to give the real product distribution under liquefaction conditions, rather than the apparent product distribution given by conventional methods. Further, application of the method shed light on liquefaction characteristics, such as the considerable conversion of coal slurry into gaseous products with the progress of liquefaction.

1. Experimental

Subbituminous Taiheiyo coal was thermally liquefied without addition of a catalyst.

1.1 Equipment

Figure 1 is a schematic diagram of the reaction

Fig. 1. Schematic diagram of liquefaction apparatus
1. Autoclave
2. Electric heater
3. Liquid-sampling cell
4. Gas-sampling cell
5. Magnetically driven stirrer
6. Thermocouple
7. Compressor
8. Pressure control valve
9. Gas holder
10. Hydrogen gas cylinder

* Received May 7, 1991. Correspondence concerning this article should be addressed to S. Sato.
apparatus (Nitto Hannooki Co. Ltd). The reactor was an electrically heated autoclave of $5.00 \times 10^{-4}$ m$^3$ inner volume with a magnetically driven stirrer. It was equipped with two sampling cells of $1.00 \times 10^{-5}$ m$^3$ inner volume that allowed sampling of the reacting mixtures from the gas and slurry phases. Impellers were mounted on the stirring stem to insure uniformity of temperature and concentration in the two phases. A helical ribbon blade was adopted for the slurry phase. It was far more effective for stirring rather viscous coal pastes than other kinds of impellers tested. An anchor impeller, moreover, was attached to the lower end of the stem to sweep near the autoclave bottom so that no solid particles might settle out. A flat blade was attached for agitation of the gas phase. A vertical temperature distribution in the gas phase could not be avoided, since any thermal insulation might have induced intolerable thermal stress over the top flange of the autoclave. A temperature distribution in the slurry phase was avoided, however, at stirring rates greater than 500 min$^{-1}$ and amounts of feed pastes below 2.00 $\times$ 10$^{-1}$ kg. Thus, to be on the safe side, 1.60 $\times$ 10 kg of paste was fed and stirred at more than 500 min$^{-1}$ in all reaction experiments.

1.2 Liquefaction procedure

The pastes were prepared at desired coal concentrations and fed into the autoclave in the constant amount described above. The autoclave was then flushed with cold hydrogen and pressurized with hydrogen up to pressures corresponding to a reaction pressure of 19.7 MPa at specified temperatures. The temperatures were controlled within an error of $\pm$ 8.00 K.

The batch reaction was started as the autoclave was heated up at a mean rate of 6.80 K.min$^{-1}$ with simultaneous stirring. After the autoclave temperature reached the desired value, sampling was carried out. Prior to sampling, the cells were flushed with hydrogen and then their internal pressures were released. Thus the great internal pressure differences between autoclave and cells forced the reacting mixtures to flow into the cells. Gas phase sampling involved problems that would cause partial condensation of gaseous products during sampling; therefore, the slurry phase alone was sampled in the present work. The reacting mixtures sampled were released into beakers. After the sampling, the cell and the lines leading the mixture to the cell were purged with hydrogen from the gas holder to avoid contamination of the resultant mixture. The pressure drop inside the autoclave after sampling was compensated by supplying hydrogen through the gas holder.

The sampling procedure described was repeated five or six times a batch. For observation of iso-thermal reaction courses, sampling was done while the autoclave temperature was kept constant during the desired times. Such temperatures and times hereafter are called reaction temperatures and times to distinguish them from heating-up temperatures and batch times. As for a nonisothermal reaction course, sampling was carried out during the heating-up period.

The reaction mixtures released into beakers were almost at room temperature, because the cell was allowed to stand at room temperature and had a heat capacity great enough to absorb the heat quickly. Evaporation was thus negligible.

Sampling was harder to do when the reaction mixtures were more viscous. In general, the lower the reaction temperature and the higher the coal concentration the more viscous was the paste. Therefore, coal concentrations in the feed paste to which sampling was applicable were up to 30 or 50 wt%, depending on whether the reaction temperature was 623 K or over 673 K. The maximum applicable number of samplings per batch depended on the amount of paste charged, the inner volume of the cell and the degree of gasification of the feed paste.

1.3 Determination of liquefaction components

A portion of each sample was provided for determination of the mineral matter (ash) concentration in the slurry phase. Each sample was mixed well so as to have a uniform concentration of solid particles. About $1.00 \times 10^{-6}$ m$^3$ of the sample was placed on a platinum boat, weighed and baked at 1073 K. The weight of the combustion residue was determined. This procedure was repeated three times and the mean weight was employed for the ash concentration determination. The accuracy of the determination was confirmed by the following experiments. A vehicle containing given weights of mineral matter resulting from combustion of the coal was subjected to reaction conditions at 623 K, where vehicle gasification was slight. The ash concentration was found to be determined within a relative error of about $\pm$ 8.00%. The slight gasification of the vehicle was ascertained by fact that pressures inside the autoclave during the experiments increased linearly with temperature.

The remaining portion of the sample was used for the determination of the other components with consecutive Soxhlet extractions. For effective extraction, the sample was mixed with a ten-fold amount of n-hexane and then sonicated for an hour prior to extraction. It was extracted in series with n-hexane, toluene and finally tetrahydrofuran (THF), or first with n-hexane and finally benzene using a glass-fiber thimble (Toyo Roshi Kaisha, Ltd., No. 86R). The final residue was baked. The former sequence
separated the sample into four components: unreacted coal (URC-T, organic THF insolubles); preasphaltene (PRA, THF solubles but toluene insolubles); asphaltene (ASP-T, toluene solubles but n-hexane insolubles); and oil (OIL, n-hexane solubles). The latter sequence produced three components: URC-B (organic benzene insolubles); ASP-B (benzene solubles but n-hexane insolubles); and OIL.

Gaseous products (GAS, components present in the gas phase under reaction conditions) were evaluated by utilizing the enrichment effect of ASH. The evaluation procedure will be described later. The enrichment effect was caused by the decrease in slurry holdup with gasification. The gasification was due to the evaporation of some portions of the vehicle and decomposition of the paste into gaseous products.

The component concentrations were evaluated on the basis of mineral matter-free coal (mmf coal). This basis, rather than a moisture- and mineral matter-free basis, was used because the moisture after reaction cannot be separated from the reaction mixtures, whereas mineral matter can be separated.

1.4 Materials

The coal, provided by Mitsui Engineering and Shipbuilding Co. Ltd., was pulverized into particles passing through a 100-mesh screen. Hydrogenated anthracene oil was employed as a vehicle. Vehicle preparation was the same as that described in our previous work8). The vehicle was thoroughly soluble in n-hexane, i.e., it fell within the OIL category. The solvents, such as THF (Kanto Chem. Co.), were similar to those described in the paper. Table 1 shows the ultimate and proximate analyses of the coal and the vehicle.

2 Theoretical Consideration of Evaluation of Component Distribution

Figure 2 shows a conceptual diagram of a batch autoclave in which the reaction is taking place. Since hydrogen absorption and slurry gasification accompany the reaction, the slurry holdup changes as the reaction progresses. Thus, the actually produced and/or consumed amounts of the components cannot be evaluated until the holdup and gasification amounts and concentrations are determined.

Mass balances at a given batch time with respect to ASH and slurry will be described below for the case where no ASH moves to the gas phase and hydrogen absorption is negligibly small in comparison with the gasification.

\[
S^0 = S + G \\
S^0 \cdot x_{ASH} = S \cdot x_{ASH}
\]

From the above equations,

\[
S = S^0 (x_{ASH}/x_{ASH}) \quad (3)
\]

\[
G = S^0 \{1 - (x_{ASH}^0/x_{ASH}) \} \quad (4)
\]

Consequently, the slurry holdup and gasification can be determined simply from the ASH concentration. The yield of each component on the mmf basis is calculated as follows:

\[
X_i = S \cdot x_{ASH} / (S \cdot x_{ASH}^0) = (x_i / x_{URC}^0) \cdot (x_{ASH} / x_{ASH}) \quad (5)
\]

where \( i \) = URCs, PRA, or ASPs.

\[
X_{GAS} = G / (S \cdot x_{URC}^0) = (1 - (x_{ASH}^0/x_{ASH})) / x_{URC}^0 \quad (6)
\]

OIL yield is evaluated with the following equation, derived under the assumption that the vehicle consists only of OIL and is not consumed.

\[
X_{OIL} = (S \cdot x_{OIL} - S \cdot x_{OIL}^0) / (S \cdot x_{URC}^0) = (x_{OIL} / x_{URC}) \cdot (x_{ASH} / x_{ASH}) - (x_{OIL}^0 / x_{URC}^0) \quad (7)
\]

Thus, a batch reaction course is obtained with consecutive samplings during the batch and application of the above equations to the reaction mixtures sampled.

In other studies, the yield was determined without consideration of the holdup change, e.g., using \( X_i = x_i / x_{URC} \) instead of Eq. (5). Moreover, disturbances which might be induced by sampling during the course of the reaction were not discussed.
3 Experimental Confirmation of Absence of Sampling Disturbance During Reaction Course

For experimental confirmation, a control experiment that induced no sampling disturbance was carried out. It was made by a modified application of the proposed method; namely, a batch with consecutive samplings was replaced by a series of batches which were evaluated by sampling once each at separate reaction times and were carried out under identical reaction conditions. Each of the batches sampled once provided a point on the reaction course without sampling disturbance. Thus, after the reaction course is observed by the proposed method, several batches for the control experiment are run along the course and then their results are compared with the course of reaction of the consecutively sampled batch. When they are made around a reaction time during which the course is most strongly disturbed, only a few batches are needed for the control experiment to show whether or not a disturbance occurs. Provided the coal decomposes at first-order rate and the sampling disturbs an isothermal batch reaction course, the course is maximally disturbed at a time from the sampling initiation of which the magnitude of order is equal to the reciprocal of the rate constant.

A course was first observed by the proposed method and the rate constant was estimated to range from $1.00 \times 10^{-2}$ to $1.50 \times 10^{-2} \text{min}^{-1}$. Hence the control experiment should be done during a period from $67 (=1/1.00 \times 10^{-2})$ to $100 (=1/1.50 \times 10^{-2})$ min. Actually, two batches sampled once each were made at 60 and 120 min. Both times were chosen so as to be as close as possible both to the above period and to the observed points on the course. Figure 3 shows an example of the results. The discrepancies between the comparison points were within experimental error. It was confirmed that little disturbance, if any, was caused the sampling.

The figure also makes clear how component concentrations vary and shows that the net amount of the components cannot be determined directly from their concentration owing to the change in slurry holdup. The holdup, estimated from the ASH concentrations using Eq. (3), is found to decrease to nine-tenths of the charged amount. This finding is important for design of liquefaction reactors, as is discussed below. The liquefaction can be taken to be a slow gas-liquid reaction that is controlled by the reaction rate in the bulk liquid. A crucial requirement for such a reaction is that adequate liquid holdup be maintained. If the reactor is designed without consideration of significant gasification, it may not perform as specified.

Fig. 3. Changes in component distribution in slurry phase and its holdup, and sampling effect on liquefaction progress at 723 K using 20 wt% coal paste, in which $x_{\text{cr}} = 0.172$, $x_{\text{OH}} = 0.800$ and $x_{\text{H2}} = 2.84 \times 10^{-2}$. The open keys are for periodic sampling, the others for sampling at specified liquefaction times.

Fig. 4. Liquefaction courses of 30 wt% coal paste observed at 693 K by two methods. The closed keys are for a previous method with a shaking autoclave and the open ones are for the present method.

4. Application of the Proposed Method and Discussion

4.1 Comparison with previous work

Figure 4 shows an example of the comparisons between reaction courses. The course from a previous study was obtained with a shaking autoclave, which was heated up to the reaction temperature in an hour.
at the same mean rate as was the present autoclave. It was cooled down to room temperature in two hours. Gas amount was determined from the weight difference between the charged paste and the liquids collected after cooling down the autoclave. The course was given after three runs of the above operation at different reaction times. The other conditions, including a reaction pressure of 19.7 MPa, were almost the same as those in the present work.

The previous course was actually nonisothermal, owing to the contribution of reaction progress during the period for cooling down the autoclave. On the other hand, the present method effectively provided a strictly isothermal course with only one run.

1) Qualitative comparison From the extent of coal decomposition the previous course appears to proceed more rapidly than the present one. Such an appearance may be due to the reaction progress involving the cooling-down period of the previous autoclave. Reaction progress of that kind did not contribute to the present course. Actually, the above consideration was found to be almost reasonable if the coal decomposition mechanism was considered.

The GAS and OIL yields in the two courses are significantly different. Similar behavior was found between experimental results reported by other workers and ours, which were obtained under experimental conditions similar to those by those workers. Such characteristics are ascribed to the observation that compounds determined as GAS were different in the two studies. At the reaction temperature, in addition to light compounds such as CH₄, C₂H₆ or C₃H₈, compounds heavier than these moved to the gas phase because of the relatively high vaporization pressure of the coal-derived liquids.

The present work determined all the compounds moving to the gas phase as GAS. Therefore it evaluated GAS in great amount at the cost of vaporized compounds which may almost fall within the OIL category. Unlike the present work, the previous study determined only the light compounds as GAS and specified the heavier compounds as OIL because of their condensation on weighing after cooling down of the autoclave. Hence the previous course was scarce in GAS and abundant in OIL.

These properties indicate that even if a coal is liquefied under almost the same conditions, the two methods give apparently different courses because the reaction results are evaluated at different gas-liquid equilibria. Further, the previous method does not always give the real OIL and GAS distribution under liquefying conditions.

2) Kinetic comparison As mentioned above, the two courses were observed eventually at different gas-liquid equilibria and differed essentially from one another in such ways as being either isothermal or nonisothermal.

Thus, the kinetic comparison should be made with consideration of these differences. To make such a comparison in detail, however, a separate study of kinetic model identification is required. Further, kinetic analysis based on the previous experimental method necessitates several additional batches as well as rather tedious nonisothermal calculations. As for URC, however, the kinetic comparison can easily be made without additional experiments or tedious calculations. The reason is that URC never moves to the gas phase and hence its measured amount does not depend on gas-liquid equilibria during sampling. Further, only experimental results with respect to URC, even if they are intrinsically nonisothermal, can kinetically be analyzed as isothermal.

Therefore, the kinetic comparison was restricted to URC. The results are shown in Fig. 4. The figure shows almost the same first-order rate constant for the two courses. In short, both courses proceeded at the same kinetic rate though they appear to be considerably different.

If reaction results obtained by the proposed method and the conventional one are to be considered simultaneously in connection with the whole reaction path involving all components, GAS and OIL amounts once evaluated by one method must be re-evaluated under other gas-liquid equilibria in the other method.

4.2 Effect of vehicle concentration

No detailed reaction characteristics, except for coal decomposition, have been studied at various vehicle concentrations. Such information is essential for a complete understanding of the vehicle's role in the reaction.

Therefore, vehicle concentration effects were experimentally studied at a reaction temperature of 723 K and concentrations ranging from 50 to 80 wt%. It was found that (1) the coal decomposition rate was significantly affected by vehicle concentration, which coincides with a previous observation, and (2) the vehicle concentration affected product distribution considerably, and higher vehicle concentrations tended to favor ASP-T and GAS yields and were not always advantageous for PRA and OIL yield.

4.3 Reaction course during preheating period and mass transfer effect on it

In any direct reaction process the coal paste must be preheated to liquefaction temperature. The reaction must proceed partially during the preheating time. Thus the reaction characteristics during this time are of interest in the design of preheaters. They also need to be examined in connection with mass transfer, because the reaction rate may be controlled by mass transfer at temperatures as low as those encountered in the preheating. Few reports
concerning this problem have been found, though some\(^6,9\) reported no effect of mass transfer at higher temperatures with stirring vigorous enough to completely disintegrate the coal particles.

Reaction courses of 20 wt% coal paste were observed during preheating time at 500 and 1000 min\(^{-1}\) as the lowest and highest stirring rates respectively. **Figure 5** shows the results. The courses likely proceeded through a series reaction in which coal decomposed sequentially to PRA, then to ASP and OIL or GAS. This behavior is similar to that in the isothermal reaction shown in Fig. 4. Therefore, the coal during the preheating time liquefied essentially in a way similar to that under isothermal conditions.

The differences in component distribution along the courses between the lowest and highest stirring rates are within the limit of experimental error. Accordingly, the reaction course during the preheating time, at least starting from 593 K, was not affected by mass transfer.

The negative yield of OIL may be a result mainly of vehicle consumption by PRA formation through the interaction with coal\(^5,12\), because the vehicle cannot decompose into GAS at the low temperatures during the initial preheating time.

**Acknowledgement**

The authors thank J. Nakamura, K. Sato, K. Sano, T. Takahashi, K. Mizusawa, M. Nitta and T. Suzuki for their kind cooperation in liquefaction experiments. They also are grateful to T. Hashimoto and M. Morita for helpful discussions about this work, and to K. Takahashi for his useful suggestion regarding the helical ribbon blade. This work was partly supported by the Sunshine Project Promotion Headquarters, Agency of Industrial Science and Technology.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>ASH</td>
<td>mineral matter</td>
<td></td>
</tr>
<tr>
<td>ASP-B</td>
<td>asphaltene separated as benzene solubles but (n)-hexane insolubles</td>
<td></td>
</tr>
<tr>
<td>ASP-T</td>
<td>asphaltene separated as toluene solubles but (n)-hexane insolubles</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>gasification amount</td>
<td>[kg]</td>
</tr>
<tr>
<td>GAS</td>
<td>gaseous products</td>
<td></td>
</tr>
<tr>
<td>(k)</td>
<td>first-order rate constant</td>
<td>[min(^{-1})]</td>
</tr>
<tr>
<td>OIL</td>
<td>(n)-hexane solubles</td>
<td></td>
</tr>
<tr>
<td>PRA</td>
<td>preasphaltene separated as THF solubles but toluene insolubles</td>
<td></td>
</tr>
<tr>
<td>(S)</td>
<td>slurry holdup</td>
<td>[kg]</td>
</tr>
<tr>
<td>(t)</td>
<td>time</td>
<td>[min]</td>
</tr>
<tr>
<td>URC-B</td>
<td>unreacted coal separated as benzene insoluble organic matter</td>
<td></td>
</tr>
<tr>
<td>URC-T</td>
<td>unreacted coal separated as THF insoluble organic matter</td>
<td></td>
</tr>
<tr>
<td>(X)</td>
<td>weight fraction on the basis of mineral matter-free coal</td>
<td>[-]</td>
</tr>
<tr>
<td>(x)</td>
<td>weight fraction in slurry</td>
<td>[-]</td>
</tr>
</tbody>
</table>

\(<\)Subscripts\(>

\(i\) with respect to a given component

\(0\) at feed conditions

**Literature Cited**