Coal Particle Disintegration at Elevated Temperatures

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INTRODUCTION

The disintegration of coal particles is a crucial first step in coprocessing and coal liquefaction reaction environments, and is a matter of concern for applications where coal particles are to be used as a catalyst support. Despite its importance, little is known about this phenomenon and few direct measurements have been reported in the open literature. Pozzobon et al. (7) conducted some preliminary experiments with a capillary view cell, in the absence of catalytic and mixing effects, and proposed a physicochemical model for particle disintegration. Their model proposes that small reagent molecules diffuse into the submicro pores of coal particles where they react rapidly with coal constituents to produce molecular species of intermediate density. These latter species are further proposed to be too large to diffuse out of the pores and the resulting pressure rise within the pores causes the particles to fracture. The model is supported by experimental evidence. For example, Pozzobon et al. (7) observed micron and submicron fragments drifting away from parent particles when suitable reagents were present in the reaction environment. The proposed mechanism is also consistent with extant coal dissolution kinetic studies, where particle size is found to be a variable of secondary importance.

Particles can be completely disintegrated at minimal conversion.

In the present work, the impact of agitation, solvent saturation, and catalyst impregnation on the mechanism or rate of particle disintegration is explored. Questions addressed include: do impregnated catalysts help or hinder the disintegration process, does saturation of coal particles with solvent (swelling) alter the disintegration mechanism, does agitation accelerate the disintegration process? We also question the suitability of coal particles per se as catalyst supports for hydrocarbon hydrogenation processes.

EXPERIMENTAL

All experiments were performed in a 50 cm³ sandwich style cell designed for a maximum working pressure of 200 bar at 700 K. The cell system is constructed of 316 stainless steel and the cell body is machined into a block of stainless steel. The sapphire windows at both ends are sealed and cushioned by graphite shims and clamped in place by stainless steel cover plates. The studs that secure the whole assembly include spring washers which compensate for differential thermal expansion effects. The cell is equipped with ten ports. During this study, three were used for pressure and temperature monitoring, and a rupture disc connection, and two for fluid inlet and outlet. The cell was manufactured by D. B. Robinson and Associates, Edmonton, Alberta.

During a typical experiment, four or five 1000 micron diameter coal particles and 20 mL solvent were loaded into the cell, which was then depressurized with an aspirator to remove air. The cell was then pressurized with gas. During experiments with mixing, gas bubbles with a 2.4 mm diameter were continually fed through the base of the cell and gas was bled from the top to maintain a target pressure. During experiments without mixing, the reactor was sealed and allowed to reach a target pressure. In all cases, the cell was heated to 700 K at 0.5 K/min and particle disintegration was recorded on video at 9 x magnification. For coal+catalyst experiments coal particles were impregnated with catalyst using a method developed by Dukhedin-Lalla et al. (2,3).

Blind Canyon and Battle River coal samples were supplied by the Pittsburgh Energy and Fuels Research Centre and by Energy, Mines and Resources Canada respectively. Proximate and ultimate analyses for the coals are shown in Tables 1 and 2. The solvents hexadecane and tetralin,
RESULTS AND DISCUSSION

Summary of Experiments and
Variables

A matrix of experiments was
established involving the following
variables and levels: coal (Blind
Canyon, Battle River), gas (hydro-
gen, nitrogen), solvent (tetralin,
hexadecane), catalyst (iron sulphate,
none), initial gas pressure (500, 800,
1000 psig), mixing (bubble injection,
one), and solvent saturation of parti-
cles (yes, no), i.e., for some experi-
ments the coal particles were left to
stand over night in solvent under
pressure but at room temperature. A
total of 18 experiments were per-
formed. In all other respects the oper-
ating conditions for these
experiments were identical. Photomi-
crographs associated with each ex-
periment are available. Some of these
are shown in Figures 1 to 12 and an
edited videotape has been prepared.

An Overview of the Experimental
Results

In general, it is worth noting
that, Battle River coal was more reac-
tive than Blind Canyon coal under the
reaction conditions employed. Thus
coil type is of importance in deter-
mining the rate of particle disintegra-
tion. However, this variable is of less
importance than some of the variables
considered below.

Experimental results which re-
examine the role of hydrogen in the
particle disintegration process (fig-
ures 1, 3 and 4) confirm previous find-
Table 1. Blind Canyon Coal Analysis

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<tr>
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<th>AS REC'D</th>
<th>DRY</th>
<th>DAF</th>
<th>DMFP</th>
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<tr>
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<td>-</td>
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<tr>
<td>Ash</td>
<td>13.17</td>
<td>13.89</td>
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<tr>
<td>Volatile</td>
<td>39.23</td>
<td>41.38</td>
<td>48.05</td>
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<tr>
<td>Fixed carbon</td>
<td>42.40</td>
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ULTIMATE ANALYSIS

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<tr>
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<td>Carbon</td>
<td>66.15 69.78 81.04 82.35</td>
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<tr>
<td>Hydrogen</td>
<td>4.80   5.06 5.88 5.97</td>
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<tr>
<td>Nitrogen</td>
<td>1.21   1.28 1.49 1.51</td>
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<tr>
<td>Total sulphur</td>
<td>0.45 0.47 0.55 0.55</td>
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<tr>
<td>Oxygen (diff.)</td>
<td>9.02 9.52 11.06 10.17</td>
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Table 2. Battle River Coal Analysis

<table>
<thead>
<tr>
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<td>Ash</td>
<td>10.53</td>
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<td>-</td>
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<tr>
<td>Volatile</td>
<td>27.06</td>
<td>36.57</td>
<td>42.64</td>
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<tr>
<td>Fixed Carbon</td>
<td>36.40</td>
<td>49.20</td>
<td>57.36</td>
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ULTIMATE ANALYSIS

<table>
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<tr>
<th></th>
<th>ASREC'D DRY DAF DMFP</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>47.13 63.70 74.27 74.27</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.25   4.39 5.12 5.12</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.95   1.28 1.50 1.50</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.40   0.54 0.63 0.63</td>
</tr>
<tr>
<td>Oxygen (diff.)</td>
<td>11.73 15.86 18.48 18.48</td>
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In summary, the conditions most favorable to coal particle disintegration include high pressure hydrogen gas and precatalyst of particles with an aromatic/hydroaromatic solvent coupled with agitation. Impregnated iron sulphate catalyst has no impact on disintegration rates whereas aliphatic solvents and inert gases appear to inhibit particle disintegration.

Mechanisms for Coal Particle Break Up

Translation of the phenomenological evidence above into mechanisms for particle disintegration is straightforward. Particle disintegration is characterized by mass transfer limited erosive breakdown where molecular hydrogen is the principal reacting species. The basic model remains unchanged from that of our previous publication (7). However, this model is incomplete and must be augmented because it fails to include solvent and agitation effects.
these species through to the particle core via diffusion through pores or directly through the coal matrix (6). If the particle is then heated, these species react with the coal matrix in much the same way as they do at the surface and the particle structure is weakened. Since some macerals are more readily penetrated with solvents or are more reactive than others, coal particles quickly become an agglomeration of sub-particles held together by thin fluid films. Under mild agitation, these films are ruptured and the much finer sub-particles which result then break up according to the basic mechanism. In the presence of an unsuitable solvent, diffusion processes and hydrogenation reaction rates are reduced and particle disintegration is retarded. With this addendum the pervious coal particle disintegration model appears to be complete.

Suitability of Coal Particles as a Catalyst Support

The experiments reported in this paper mimic the behavior of a slow preheater for hydrogenation processes. More typically the heat up time would be six minutes rather than two hours. Thus the impact of mass transfer effects on particle disintegration would be even more pronounced and the particles would be more durable at elevated temperatures than indicated by the experiments. As particle disintegration rates accelerate above 700 K, particles per se do not persist beyond five to ten minutes at elevated temperatures in hydrogenation reaction environments. In such cases, the particles merely act as a catalyst dispersant rather than as a support, and other dispersant methods may prove equally effective. The application of coal particles as a catalyst support must be restricted to reaction environments where reaction time is short, reaction temperature is
relatively low, hydrogen partial pressure is low and hydrocarbon liquids are primarily aliphatic in nature.

CONCLUSIONS

Coal particle disintegration in solvents at elevated temperatures is characterized by the erosive cleavage of micron and submicron particle fragments from parent particles. The rate of particle disintegration is limited by molecular hydrogen transfer to/within coal particles but is unaffected by the presence of impregnated catalysts. Saturation of particles with a hydroaromatic solvent coupled with agitation contributes a complementary breakage mechanism where large reacting coal particles are cleaved into random sized sub-particles which are in turn subject to erosive cleavage. As coal particles are not durable at elevated temperatures, they can act more readily as dispersants for catalysts than as catalyst supports.

ACKNOWLEDGMENTS

We thank the Department of Metallurgy and Material Science at the University of Toronto for the use of equipment and gratefully acknowledge financial assistance provided by CANMET through DSS contract #64SS.23440-0-9167.

LITERATURE CITED


