

TITLE: STUDY OF SOLVENT AND CATALYST INTERACTIONS IN DIRECT COAL LIQUEFACTION

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ABSTRACT

OBJECTIVES

1. To clarify the roles of the solid catalyst and the solvent in the direct liquefaction of coal.
2. How does the solvent mediate between the coal and the catalyst?
3. Investigate the composition of Volatile Matter in coal and coal liquids by thermogravimetric/mass spectrometry and determine how it varies with coal rank and process.

ACCOMPLISHMENTS TO DATE

An open question concerning the role of the solid catalyst in direct coal liquefaction is whether intimate contact between the catalyst and the coal particles is required. To answer this question, the solid catalysts were put in stainless steel baskets which were permeable to solvent and coal liquid but not to the solid coal. Several such baskets were constructed of stainless steel with hole sizes from 0.5 and 2,0 ~ to 30 mesh. The baskets were suspended in our short contact time batch (SCTBR) reactor and the liquefaction process carried out as has been done without the basket. Runs were made using sulfided amocat and shell Ni/Mo on alumina catalysts and tetralin and methylnaphthalene and decalin solvents. These showed that with tetralin, liquefaction occurred with and without catalyst but with greater conversion with catalyst present. It appears therefore that even with separation of the coal and catalyst, there is mass transfer between the catalyst and the coal via the solvent.

A technique has been developed for studying the composition of the Volatile matter in coal using Thermogravimetry-Photoionization Mass Spectrometry. We had previously shown that there is a direct correlation between the maximum temperature of volatiles evolution (by TGA) and the coal rank by vitrinite reflectance. Now we have been able to show that the composition of the volatile matter changes with rank and that the rank can be predicted by the composition of the volatile matter.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

A clearer understanding of the roles of the solid catalyst and the solvent in direct coal liquefaction should lead to higher yields, conversions and greater productivity of coal derived fuels at lower costs. This work which shows that it is not necessary to finely grind the catalyst to get good conversion and yield is important. The role of the solvent also is important.

The ability to analyze the molecular constituent of Volatile matter by TG/MS in coal and in coal liquids is important in better understanding the liquefaction process.

PLANS FOR THE COMING YEAR

. With the equipment to run liquefactions with various catalysts and solvents, a program is underway for selection of catalyst and solvent combinations to get the greatest productivity at the lowest cost in direct coal liquefaction. TG/MS will be used to evaluate the products.

• The Thermogravimetry-Photoionization Mass Spectrometry will be investigated as a tool for determining the mode of catalyst inactivation.

ARTICLES PRESENTED

JOURNAL ARTICLES (PEER REVIEWED)

He Huang, Keyu Wang, Shaojie Wang, Michael T. Klein and William H. Calkins
"Studies of Coal Liquefaction at Very Short Reaction Times 2" Energy and Fuels
Vol 12, number 1 pps.95-101 (1998)

He Huang, Shaojie Wang, Keyu Wang, M. T. Klein, Alan Davis and W.H. Calkins
"Thermogravimetric and Rock-Eval Studies of
Coal Properties and Coal Rank" Energy and Fuels Vol 13, Number 2 pps. 396-400 (1999)

David Zoller, Murray V. Johnston, Jasna Tomic, Xiaogong Wang and William H. Calkins
"Thermogravimetry-Photoionization Mass Spectrometry of Different Rank Coals"
Submitted to Energy and Fuels

Title:

A Study of Solvent and Catalyst
Interactions in Direct Coal Liquefaction

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Summary

An open question concerning the role of the solid catalyst in direct coal liquefaction is whether intimate contact between the catalyst and the coal particles is necessary. Mass transfer considerations suggest such contact between two solids in a liquid medium is difficult to achieve. However, much research effort has been devoted to producing ultrafine catalyst particles in order to get better contact between the catalyst and the coal. In an effort to answer this question and to study catalyst solvent interactions, several baskets were constructed of stainless steel with hole sizes from 0.5~, 2.0~, and 50~(30 mesh). The baskets some filled with 1-2mm x 5-10mm pellets of sulfided Ni/Mo on alumina catalyst were inserted into our short contact time batch reactor and coal liquefactions were carried out. The 0.5~ basket limited the flow of the solvent too much for adequate kinetic studies to be carried out. The 30 mesh basket operated satisfactorily although a small amount of coal leaked into the basket. The 2~ basket worked well.

The reactor was charged with 4 grams of illinois #6 (50 to 150 mesh) coal in 30 grams of solvent. Tetralin, 1 methylnaphthalene, and decalin were used as solvents. In each case, the runs were made with an empty basket as well as a basket charged with sulfided amocat or shell Ni/Mo on alumina catalyst. The runs were made at 420EC for 30 minutes. The product was discharged and quenched and the solvent removed. Conversion of coal to coal liquid was followed by determination of the ash content of the residue by TGA. Compositions of the volatile portions of the coal liquid were determined by TG/MS.

It is interesting to note that the liquefaction in tetralin gave higher yields in the presence of catalyst (amocat and shell) in the basket than when the basket was empty. This supports our view that intimate contact between the coal and catalyst is not necessary. We suppose the catalyst is interacting with the coal through the solvent. This is currently being investigated by using various other solvents (e.g. decalin, methyl naphthalene etc.).

A recent thermogravimetric (TGA) study of a wide variety of coals has shown that volatile matter as defined by ASTM is evolved over a relatively narrow temperature interval (100 - 120°C). The peak temperature of volatiles evolution was found to increase systematically with coal rank, as there is a very strong correlation with vitrinite reflectance. It was desired however to determine the actual composition of the volatile matter and also the volatile portions of the coal liquefaction products described above. Mass spectrometry is a useful method for identification of products evolved during coal pyrolysis as it provides the ability to identify individual compounds (by mass) from a complex distribution of evolved products. Coupling a TGA with a Reflectron time-of-flight mass spectrometer equipped with an infinity 40 - 100 ND:YAG laser (10.49eV) for "soft" ionization with minimum fragmentation, provided us with a mass spectrometer analysis of the volatile matter of the raw coal and of the coal liquefaction products. In the raw coals, the mass spectra of some 20 different coals of a range of ranks were determined. Overall, the relative amounts of oxygen containing compounds such as C.H₂O, phenols and dihydroxybenzenes decrease with rank. In addition, the relative amounts of aromatic hydrocarbons such as naphthalenes, phenanthrenes, and pyrenes increase with increasing coal rank. Throughout the range of ranks studied, olefins (propylene, butenes etc) were produced, suggesting the cracking of connecting links between aromatic groups in the coal structure. TG/MS analyses were run on coal liquefaction products produced with and without the amocat catalyst in the reactor basket. It was interesting to note that the coal residue gave very similar mass patterns for the volatile matter, whether catalyst was present or not, although more volatile matter was produced with the catalyst present.