

## A NOVEL SHORT TIME REACTOR SYSTEM FOR STUDYING THE INITIAL STAGES OF DIRECT COAL LIQUEFACTION

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Keywords: short contact time reactor, DBE conversion, coal liquefaction

### ABSTRACT

Study of direct coal liquefaction at short contact time can provide insight into the chemical and physical processes involved at low conversions, before the occurrence of significant secondary degradative and retrogressive reactions of the liquefaction products. However, it has been difficult in the past to produce well-defined, short reaction time samples for in-depth analysis. To achieve this, a novel bench scale reactor was designed and built. The characteristics of the reactor system are as follows. The coal-organic solvent liquid slurry is driven into a reactor, which is already at reaction temperature, through preheater tubing using a high-pressure gas. Preliminary tests show that this can be accomplished in less than one second, and the desired reaction temperature of the process stream is achieved within approximately 0.3 seconds. The injected slurry is agitated by gas bubbles introduced through the slurry from the bottom of the reactor. The quenching process is performed in a similar way and accomplished in less than one second. The product stream cools down to about 25 °C in approximately 0.3 seconds. The preliminary operating results on this unit for conversion of model compound, direct coal liquefaction, and conversion of coal-derived resids have been reported in this paper.

### INTRODUCTION

In the liquefaction of coal, as in many other high-pressure and high-temperature reactions, important information concerning the controlling chemical and physical processes can be obtained through study at the very early stages, before complicating secondary reactions occur. The major experimental challenge is to bring the system up to the reaction temperature and pressure in a time frame less than that required for the physical and chemical processes to start to occur. It is also important to choose an appropriate method to agitate the reactor contents to maintain uniforms of temperature and concentration.

In most laboratory high pressure equipment used to run direct coal liquefaction, such as tubing bombs or autoclaves, the heat up and cool down times of the massive equipment required to hold the pressure are long compared to the times involved in the reactions themselves. A representative temperature profile for the tubing-bomb reactor is shown in Figure 1. The resulting long heat up and cool down times obscure fundamental interpretation of the results, and do not allow practical process studies to be made at short reaction times. The common ways to agitate the reactor system are either stirring or shaking. To do this requires complicated and expensive equipment, particularly on a very small laboratory scale (ca. 30 grams). This also makes rapid sampling difficult. Thus, a reaction system at constant temperature and pressure, capable of sampling at very short reaction times (a few seconds up to 30 minutes or longer) and agitating in a simple way, is needed. Such a novel Short Time Batch Reactor (STBR) has been devised and built in our

laboratory, and tests of this apparatus for studying conversion kinetics of model compounds, coal-derived resids, and coal liquefaction are underway. Herein we report on the preliminary operating results of this unit.

## EXPERIMENTAL

### Apparatus

An empty batch reactor illustrated in Figure 2 is immersed in a sand bath and brought up to the desired reaction temperature. Using high pressure gas, the reaction mixture under study is driven into the reactor from a small blow case through preheater tubing, which is also at reaction temperature. Tests show that this can be accomplished in less than one second. Because only small quantity (about 30 grams in our present unit) of the reaction mixture is heated during injection in the relatively massive preheater tubing, the desired reaction temperature is achieved within approximately 0.3 seconds. The reaction mixture is then agitated by gas bubbles injected through the slurry from the bottom of the reactor. The degree of agitation is controlled by the exit gas flow rate from the top of the reactor. At a selected time, the reactor contents are driven out of the reactor into a cold receiver through a precoolers with high pressure gas. Both the receiver and precoolers are immersed in a water bath. This process is also accomplished in less than one second, and the cooling of the product mixture to about 25°C is achieved in approximately 0.3 seconds.

The details of the reactor system are shown in Figure 3. The heating bath used is a Techne IFB-52 industrial fluidized sand bath, which maintains a reaction temperature of  $\pm 2^\circ\text{C}$ . The 30 cm<sup>3</sup> reactor is capable of containing 17 MPa (2500 psi) pressure at temperatures up to 550 °C. The tubing used for preheater and precoolers was 1/4" 316 stainless steel with wall thickness at 0.035". The lengths of the preheater and precoolers were both about 21 feet. Since a gas (e.g. hydrogen or nitrogen) is bubbled through the reaction mixture under pressure and out through a let-down valve, a small, water-cooled condenser above the reactor and a disengaging space above it before the let-down valve are necessary to avoid loss of solvent or other low boiling components.

### Reaction Temperature Profile

A time-temperature profile for a mixture of 89% tetralin, 1% biphenyl, and 10% dibenzylether (DBE) is shown in Figure 4. At the time of injection, the reactor temperature dropped 5 - 8 °C, but it recovered to sand bath temperature within 30 seconds. This temperature drop may be reduced by longer preheater tubing.

The excellent time-temperature profile of Figure 4 is due to the preheating of the comparatively massive empty reactor and the preheater tubing and fittings prior to  $t = 0$ . This allows the only thermal transient to be focused on the reaction mixture.

### Sample Recovery

The amount of material recovered from the reactor when it is driven from the system depends on the surface area of the entire apparatus. This is because surface holds up liquid for wetting. The surface areas of the preheater and precoolers are the bulk of that involved, and therefore there is a trade off between the reaction temperature drop on injection and the degree of recovery. For that reason, the longer the preheater, the smaller the reaction temperature drop on injection, but the lower the recovery. The viscosity or fluidity of the sample stream also influences the recovery. For the process streams studied thus far, recoveries have varied from 75 to 85 %. Because of the hold-up of some of the reaction mixture on the walls of the reactor and preheater and precoolers tubings, 100% recovery of the reaction mixture is not practical. This means that analytical methods must be available

to follow the course of the reaction with aliquots. This has not been a limitation for the reactions studied thus far. However, if better material balances are required, the first sample can be supplemented with solvent washes of the system, and further quantities of the reactant recovered by solvent removal in a rotovapor.

#### Cleaning System

The reactor system can be cleaned in place by a series of suitable solvent washes. The number of the washes required will depend on the reactions being studied.

### **PRELIMINARY RESULTS**

#### Conversion of Model Compound

Solutions of model compounds, such as dibenzylether in tetralin, have been run in this equipment to investigate its performance. A temperature profile of the reaction has already been shown as Figure 4. Approximately 85% of the reaction mixture was recovered. Benzaldehyde, benzyl alcohol and toluene were the principal products as shown by GC-MS. A kinetic curve for the reaction under 1000 psi  $N_2$  at 375 °C is shown in Figure 5. Excellent fit to first-order kinetics with  $k_{DBE} = 8.78 \times 10^{-4} \text{ s}^{-1}$  was found.

#### Coal Liquefaction

Mixtures of 25% Wyodak Black Thunder coal in tetralin were run in this apparatus to begin to study the liquefaction process itself at very low conversions. A typical temperature profile at 380°C over a two minute interval is shown in Figure 6. Samples could be taken at as short a reaction time as 10 seconds, with confidence that the desired reaction time at temperature was achieved. No difficulty was encountered in driving the reaction mixture in and out of the reactor. Recovery of the reaction mixture was about 80%.

#### Conversion of Coal-Derived Resid

Initial studies with this new reactor are being devoted mainly to investigation of the conversion kinetics of coal-derived resids. The compositions of the coal derived resids being studied are shown in Table 1. Mixtures of the resid, in various concentrations with tetralin, such as 1:2 and 1:3, and sometimes with added catalyst, are heated sufficiently to become fluid, and then charged to the blow case which is maintained sufficiently warm with heating tape to keep them fluid. They are also agitated in the blow case with bubbling hydrogen gas. The charge is then driven into the reactor with 1500 psi hydrogen and the reactor agitated again with bubbling hydrogen. The resids are solid materials at room temperature, and contain up to 20% mineral matter. They therefore present a rather viscous mixture, even when diluted with tetralin and heated to become relatively fluid. Reactions have been run at 1500 psi and 410 °C. Recovery of the reaction mixture has been about 75%.

### **SUMMARY AND CONCLUSIONS**

This reactor system (STBR) should have broad applicability to fuel science problems and many other high-pressure, high-temperature reactions of organic or inorganic systems where small-scale experiments for kinetic measurements are needed. Complex reactions where secondary reactions set in at an early stage can be studied in this type of reaction system at very low conversions.

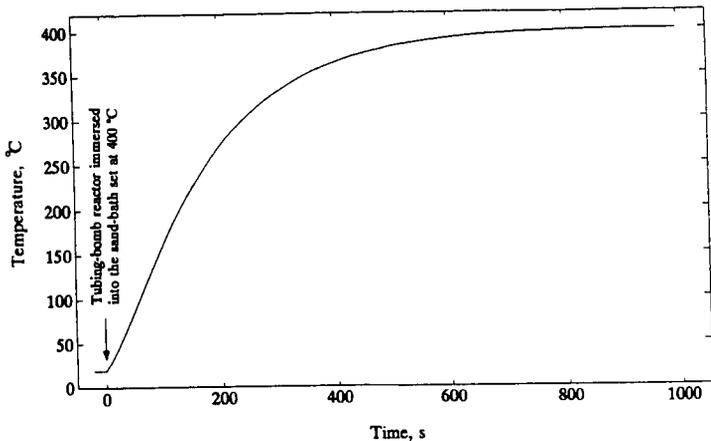


Figure 1 Time-Temperature Profile for a Tubing Bomb Reactor

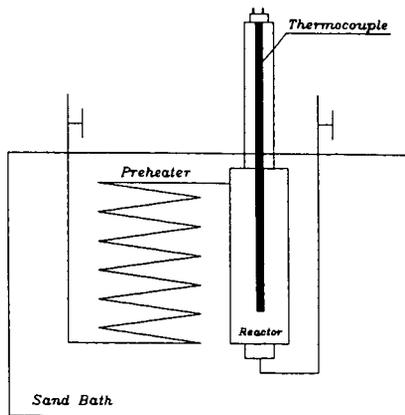


Figure 2 Batch Reactor (STBR) for Studying the Initial Stages of Direct Coal Liquefaction

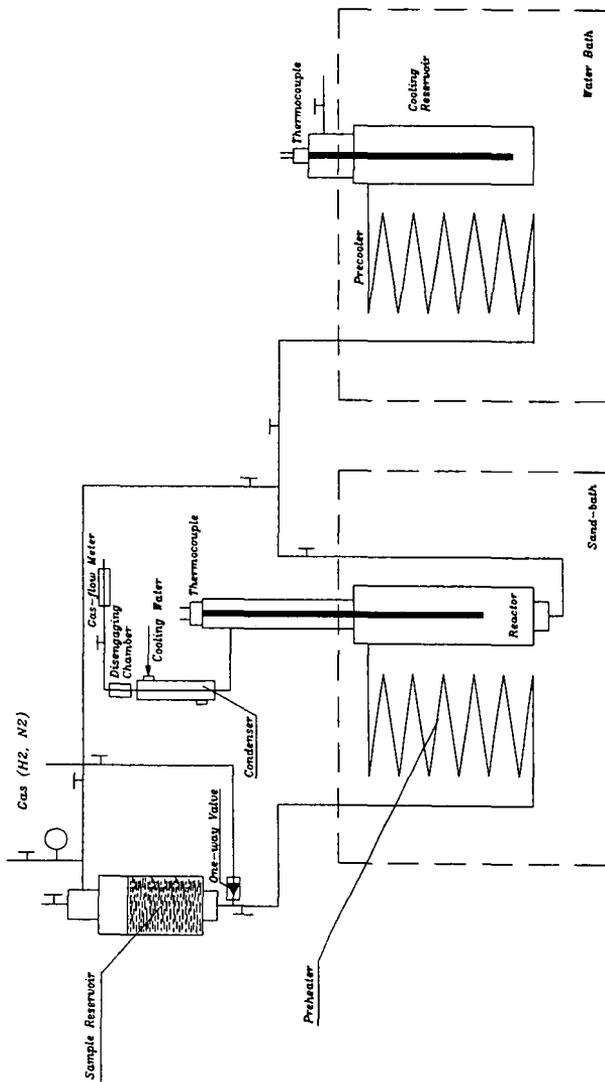


Figure 3 Apparatus for Direct Coal Liquefaction at Short Contact Times

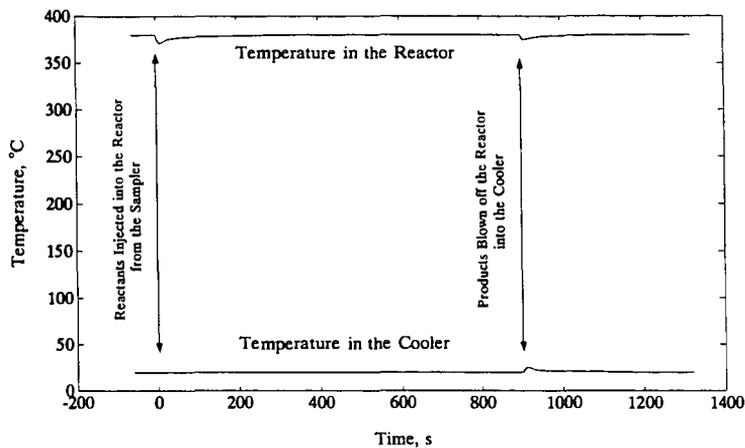


Figure 4 Time-Temperature Profile for a Typical DBE Conversion Run

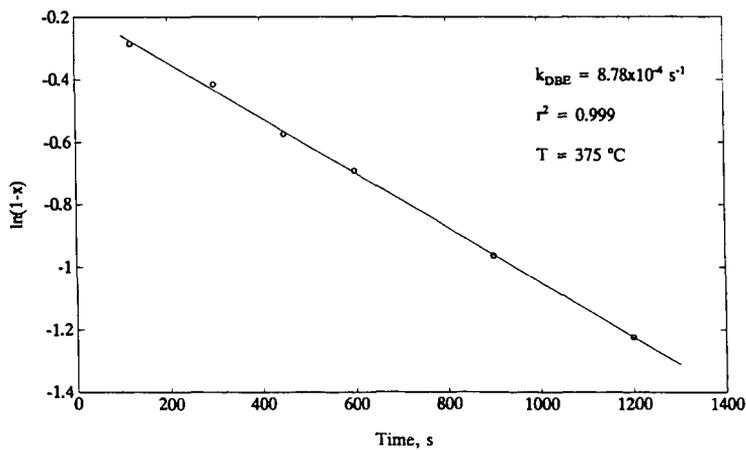


Figure 5  $\ln(1-x)$  vs. Time for DBE Conversion in Tetralin

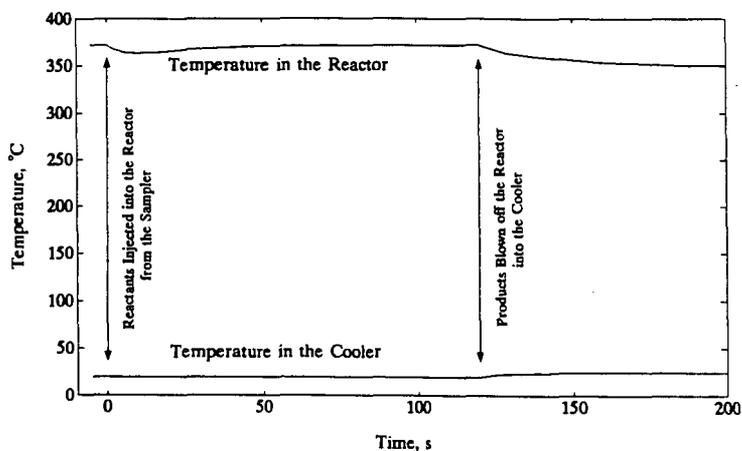


Figure 6 Time-Temperature Profile for a Typical Short Time Coal Liquefaction Run

Table 1 The Compositions of the Coal-Derived Resids

	Resid 1 <sup>a)</sup>	Resid 2 <sup>b)</sup>
<b>Ultimate:</b>		
Ash, wt%	10.21	16.67
C, wt% MAF	90.24	91.03
H, wt% MAF	6.39	6.56
N, wt% MAF	1.05	1.15
S, wt% MAF	1.49	0.09
O (by diff.), wt% MAF	0.83	1.17
<b>Proton Distribution (% , pyridine-soluble basis):</b>		
Condensed Aromatics	27.8	27.2
Uncondensed Aromatics	3.8	6.8
Cyclic Alpha	21.2	18.3
Alkyl Alpha	9.6	8.8
Cyclic Beta	15.5	13.6
Alkyl Beta	13.4	16.6
Gamma	8.7	8.7
<b>Insoluble Organic Matter in Pyridine (wt%):</b>		
	6.28	13.9

a) Feed coal: Pittsburgh seam Ireland mine, Wilsonville Run 259 of V1067 at 2nd stage product;

b) Feed coal: Wyodak abd Anderson seam Black Thunder mine, Wilsonville Run 260 of V1067 at 2nd stage product;