

## ON-LINE GC/MS ANALYSIS OF HIGH PRESSURE CONVERSION REACTIONS OF MODEL COMPOUNDS FOR COAL-DERIVED LIQUIDS

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### INTRODUCTION

Direct coal liquefaction involves complex and insufficiently defined chemical reactions. In order to improve direct coal liquefaction processes, it is necessary to improve our understanding of key chemical reactions. Unfortunately, due to the high pressure and high temperature requirements of most coal liquefaction processes, real-time on-line reaction monitoring by advanced spectroscopic and/or chromatographic techniques has generally been impossible until now. Thus, relatively little is known about the precise reaction pathways as well as the intermediate reaction products involved. This is particularly true for conversion reactions carried out in batch reactors such as autoclaves. Due to the relatively long residence times primary reaction products formed in batch type autoclaves are quite susceptible to secondary, or even tertiary reactions. Consequently, real-time on-line monitoring experiments are needed to elucidate reaction pathways in autoclaves.

Although several on-line systems have been developed for coal conversion at near-ambient pressure or high vacuum conditions [1-4], there are no reports of on-line chromatography/spectroscopy based systems built for monitoring high pressure conversion reactions. Therefore, the development of a direct GC/MS interface for near-real time analysis of high pressure reaction products, while minimally disturbing the reaction process, has been undertaken in our laboratory.

It is well established that coal contains fused aromatic and hydroaromatic ring clusters, composed of an average of two to four condensed ring units, connected by various alkylene, ether, sulfide and direct (Ar)C-C(Ar) bridges [5]. Liquefaction reactions are primarily thought to involve these connecting bridges, especially ether linkages and alkylene linkages [6]. In recent years, a number of workers [7-17] have subjected coal-model compounds to various coal conversion conditions in order to confirm that certain coal structures are reactive during coal conversion and to infer the conversion mechanisms of real coals from mechanisms determined for such compounds.

The present paper reports the design and testing of a newly developed on-line GC/MS monitoring system for high pressure reactions and its application to the investigation of hydrogenation and hydrodeoxygenation (HDO) of model compounds, such as diphenyl methane and dibenzyl ether, under both catalytic and thermal conditions.

### EXPERIMENTAL

**Instrumental Design:** Figure 1 shows that the on-line system consists of: (1) a 50 ml flow-through micro-autoclave reactor (Autoclave Engineers Inc.), with a continuous stream of mixture feed flowing through a preheater, entering the reactor from the bottom, and continuously sweeping solubilized products into a collecting reservoir; (2) a pressure reduction line (15  $\mu$ m i.d. fused silica capillary) which reduces the pressure from about 1650 psig to ambient at a mass flow of approximately 1 mg/min for toluene while minimizing dead space at the high pressure end and minimally disturbing the reaction process; (3) a novel automated vapor sampling (AVS) inlet developed at the University of Utah, Center for Micro Analysis and Reaction Chemistry (U.S. Patent No. 4,970,905) for diluting

and pulsed sampling of ambient vapor sample streams; and (4) a GC/MS system with a 1 m long, 150  $\mu\text{m}$  i.d. fused silica capillary "transfer line" GC column directly coupled to a Finnigan Mat Ion Trap Mass Spectrometer (ITMS) with tandem MS capabilities and electron ionization (EI) as well as chemical ionization (CI) options.

**Materials:** Diphenylmethane, dibenzyl ether, decalin and biphenyl, were obtained from Aldrich Chemical Co. as G.R. grade without further purification. A commercial catalyst,  $3\text{Co}8\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ , was sulfided before use for the reaction. A protonic acid catalyst,  $\text{FeCl}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ , was prepared by means of a special impregnation technique in this laboratory.

**Experimental procedure:** About 300 ml of a mixture containing 10%(wt) feed, 86% solvent (decalin) and 4% internal standard (biphenyl) were used for each experiment. Under catalytic reaction conditions, about 1 g of the catalyst was placed in a self-containing basket with 52 wire mesh. The liquid flow was about 30 ml/hr after the first reactor fill with feed mixture. The reactor was pressurized at 1600 psi with a continuous  $\text{H}_2$  supply. After analysis start-up, normally 10 samples were taken at 2 min/sample at ambient temperature for checking system stabilization. Then the GC/MS was started at the same time as the reactor started heating. The reactor temperature was recorded for each sample. After the reactor reached the reaction temperature, the reaction time was recorded. Detailed parameters for each reaction are listed in Table 1. Both reactor temperature and reaction time effects will be discussed.

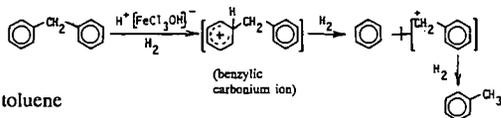
## RESULTS AND DISCUSSION

**On-line system function:** Aside from occasional plugging of the 15  $\mu\text{m}$  i.d. capillary pressure reduction line and the protective 2.0 and 0.5  $\mu\text{m}$  frits the system exceeded design specifications with regard to GC/MS performance, especially isothermal GC results (note the separation of decalin isomer peaks in Figure 2) and dynamic range (solvent peaks representing > 80 % of the reactor contents were as readily measurable as small product peaks representing less than 100 ppm thus establishing an effective dynamic range >  $10^4$ ). As also demonstrated in previous work, the combination of automated pulsed vapor sampling and short column capillary "transfer" line GC enabled repetitive recording of complete isothermal GC runs at 1-4 minute intervals. Moreover, the transfer time of nonretained sample components between reactor and detector was found to be less than 1 minute. In short, the system shown in Figure 1 is capable of detecting minute changes in sample composition in a time which is short compared to typical reaction times in autoclave reactors.

**Diphenylmethane:** Figure 2 shows the reactor temperature effect on diphenylmethane decomposition under thermal and acid-catalyzed reaction conditions. As seen, the first products can be detected at about 330°C for the catalytic reaction, but not for the corresponding thermal reaction (even at about 350°C). Kinetic profiles of the effect of reaction time on the decomposition of diphenylmethane at thermal and catalytic reaction conditions at 350°C are illustrated in Figure 3. As expected, the concentrations of the products and the feed are increasing and decreasing, respectively, as a function of reaction time for both thermal and catalytic reactions. At 350°C, conversion yield at the equilibrium stage (flow reactor!) is about 50% of the feed for the acid-catalyzed reaction, whereas the thermal reaction produces detectable products by GC/MS, but achieves a very low conversion yield, which is consistent with previous results [15,17]. Figure 4 shows typical single ion chromatograms with the corresponding mass spectra of the decomposition product of diphenylmethane (benzene, toluene, and xylene) under catalytic reaction conditions. Figure 5 demonstrates the concentration of benzene, toluene and xylenes as a function of reaction time under catalytically controlled conditions. Obviously, benzene is the dominant product, whereas the concentration of toluene is increasing with reaction time, and xylene concentrations attain only about 1% of the benzene concentration. The results infer that  $\alpha$ -bond cleavages are preferable under the

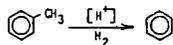
acid-catalyzed conditions which agrees with other results [11]. That the active form of the metal chloride is aqua complex [18],  $H^+[MCl_4OH]^-$ , has been considered. Thus, the mechanism of diphenylmethane decomposition under the acid-catalyzed condition is proposed as follows:

Main Reaction (hydrodealkylating cleavage of the  $\alpha$ -bond)

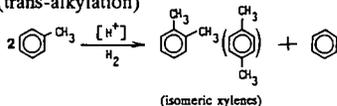


Secondary Reactions of toluene

(a) hydrodealkylation



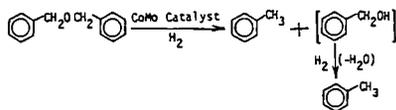
(b) disproportionation (trans-alkylation)



The rate-limiting step in the overall process is protonation of diphenylmethane to form an intermediate carbonium ion, which undergoes  $\sigma$ -cleavage to yield benzene and toluene. The small extent of secondary reactions of toluene can not be avoided under the acid-catalyzed reaction condition.

In the thermal reaction, toluene is the most important product and the ratio of toluene to benzene shows no clear trend with reaction time. A free radical mechanism is suggested. Due to very low conversion yields, the reaction pathway of diphenylmethane under the thermal conditions is not discussed.

**Dibenzyl Ether:** Figure 6 illustrates dibenzyl ether decomposition under both thermal and catalytic reaction conditions. This reaction proceeds at much lower temperatures than the diphenyl methane decomposition reaction, due to the bond energy differences listed in table 2. Figure 7 shows the kinetic profiles of the decomposition of dibenzyl ether under both thermally and catalytically controlled reaction conditions. The conversion of dibenzyl ether under catalytic reaction conditions is approximately 96%, as opposed to 30% under thermal reaction conditions. The GC/MS results reveal six products, namely: benzene, toluene, benzaldehyde, dibenzyl, 4-methyl diphenyl methane and 2-methyl diphenyl methane, from the thermally controlled reaction, while only one product, toluene, is observed from the catalytically controlled reaction. This implies that the reaction pathways under both conditions are different. The thermal decomposition of dibenzyl ether has been well defined following the free radical mechanism [8-10]. The reaction pathway of the HDO reaction of dibenzyl ether in the presence of a sulfided  $3\text{Co}8\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  catalyst is as follows:



The benzyl alcohol intermediate has been observed as the only intermediate at temperatures between 140-260°C in the presence of the same type of catalyst (3Co8Mo) at 1000-1500 psig  $\text{H}_2$  [19]. Due

to the more severe conditions under which our experiment was performed (300 C), the intermediate benzyl alcohol was not detected.

## CONCLUSIONS

A newly developed, on-line GC/MS monitoring system for high pressure reactions performed reliably. This represents a significant over conventional off line methods and should facilitate elucidation of the mechanisms and kinetics of coal liquefaction.

The results obtained suggest that the protonic acid catalyst,  $\text{FeCl}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ , acting as an aqua complex,  $\text{H}^+[\text{FeCl}_3\text{OH}]$ , causes cleavage of the  $\alpha$ -bond in diphenylmethane to produce approximately 50% each of benzene and toluene, whereas very low product yields (< 1 %) are observed in the absence of a catalyst.

The decomposition of dibenzyl ether under catalytic conditions is almost complete (96%). The only product, toluene detected, under such conditions reveals that an HDO reaction occurred. The thermal reaction mainly breaks C-O bonds by a free radical mechanism.

## ACKNOWLEDGEMENT

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TABLE 1  
EXPERIMENTAL CONDITIONS

Reactor Conditions:	
- Pressure	1600-1650 psig
- Feed Flow Rate	30 ml/hr
- Reaction Gas	Continuous flow H <sub>2</sub> 50 sccm
- Heating Speed	ambient--> 300°C in ~18 min
- Final Reaction Temperature	350°C for diphenylmethane, 340 and 300°C for dibenzyl ether under thermal and catalytic conditions, respectively
- Catalyst	~1 g sulfided 3Co8Mo/γ-Al <sub>2</sub> O <sub>3</sub>
Pressure Reduction Line Conditions:	
- Temperature	175°C
- Pressure	1600-1650 psig--> ambient
Sample Inlet Conditions:	
- Temperature	270°C
- Pressure	ambient
- Dilution He Flow Rate	100 ml/min
- Carrier Gas He Flow Rate	40 ml/min
- Sampling Valve Flow Rate	43 ml/min
- Bleed Flow Rate	10 ml/min
- Sampling Pulse	550 ms at 2 min intervals
Transfer Line Conditions:	
- Column	1 m x 150 μm i.d. coated with 0.12 μm CP-SIL 5CB
- Temperature	105°C
- Pressure	ambient -->10 <sup>-6</sup> torr
MS Conditions:	
- Pressure	10 <sup>-6</sup> torr
- Ion Trap Temperature	96°C
- Ionization	electron impact (with automatic gain control)
- Spectrum Scanning Speed	4 spectra/s
- Mass Range	m/z 50-100

TABLE 2  
PROPERTIES OF THE MODEL COMPOUNDS SOLVENT AND INTERNAL STANDARD

Name	Structure	Molecular Weight	Boiling Point (°C)	BDE (Kcal/mol)
diphenylmethane	ph-CH <sub>2</sub> -ph	168	264	350 <sup>a</sup> ,339 <sup>a</sup>
dibenzyl ether	phCH <sub>2</sub> -O-CH <sub>2</sub> ph	198	298	330 <sup>b</sup>
diphenyl	ph-ph	154	256	480 <sup>c</sup> ,485 <sup>a</sup>
decalin		138	187.1-196.4	--

- a - Ross, D.S. et al., in: *Coal Liquefaction Fundamentals*, (Whitehurst, D.D., ed.), 1980, ACS Symposium Series 139, p. 303.  
 b - Schlosberg, R.H., et al., *Fuel*, 1981, 60, 202.  
 c - Vernon, L.W., *Fuel*, 1980, 59, 103.

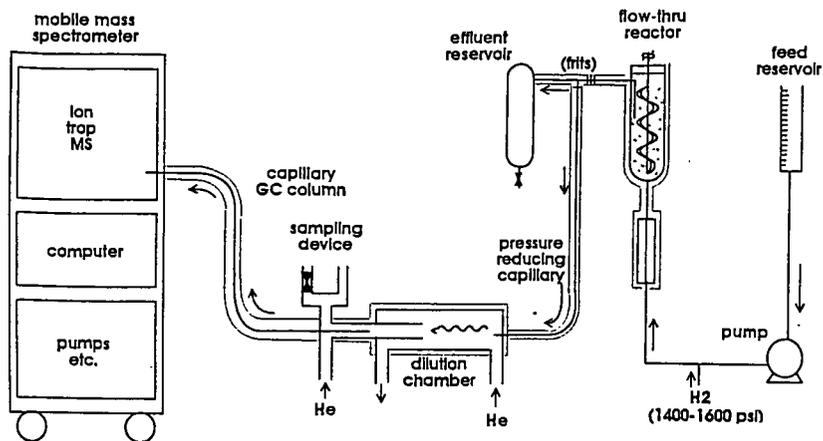


Figure 1. On-line GC/MS monitoring of high pressure reactor.

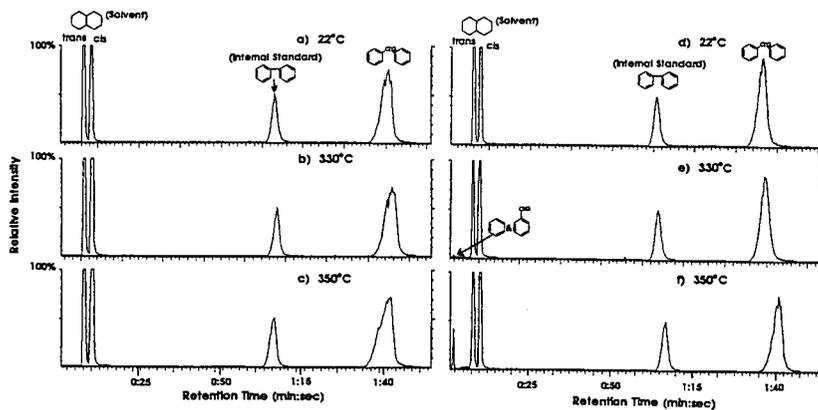


Figure 2. Total ion chromatograms of diphenylmethane at different reactor temperatures under thermal (a-c) and catalytic (d-f) conditions.

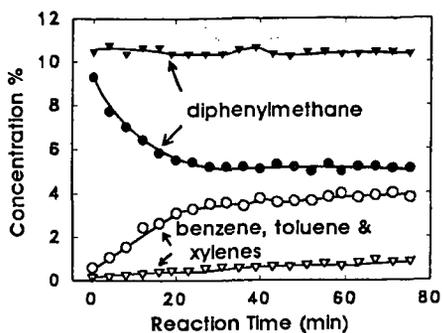


Figure 3. Kinetic profiles of the decomposition of diphenylmethane at 350 C under thermal and catalytic conditions.

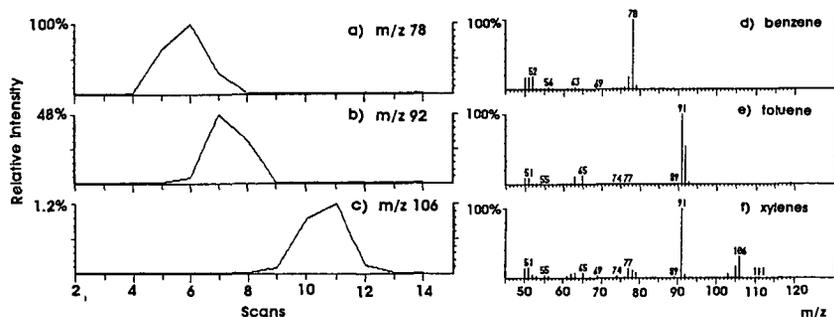


Figure 4. Typical single ion chromatograms (a-c) and corresponding mass spectra (d-f) of the products from the decomposition of diphenylmethane under catalytic conditions.

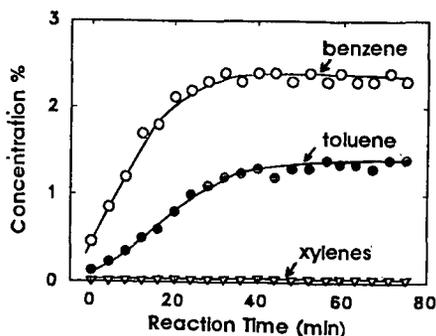


Figure 5. Relationship between reaction time at 350 C and the concentrations of the products from the decomposition of diphenylmethane under catalytic conditions.

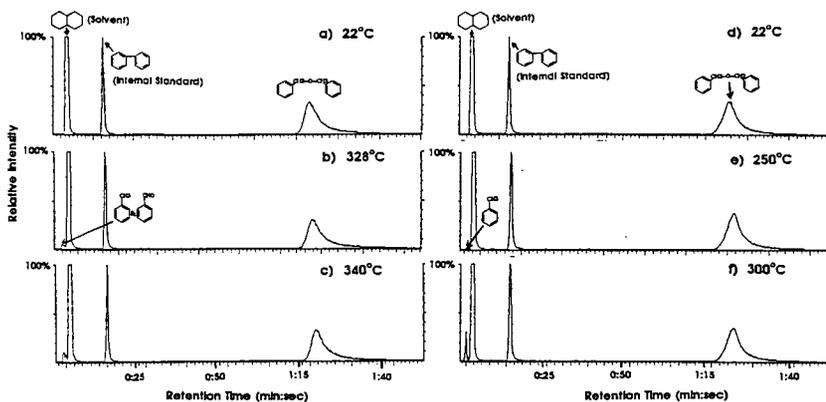


Figure 6. Total ion chromatogram of dibenzylether at different reactor temperatures under thermal (a-c) and catalytic (d-f) conditions.

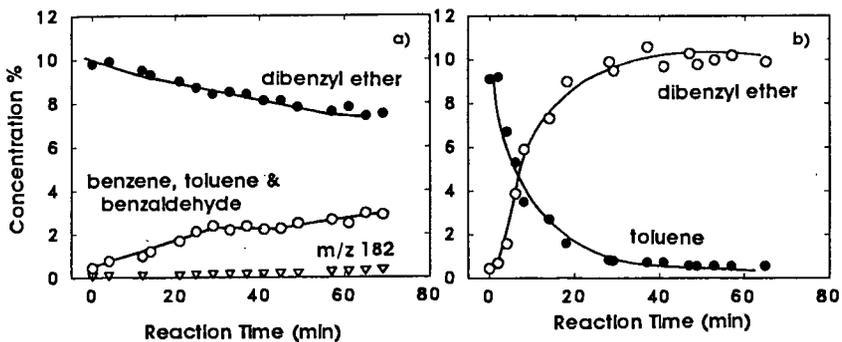


Figure 7. Kinetic profiles of the decomposition of dibenzylether under thermal (a) and catalytic (b) conditions.