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**DEVELOPMENT OF FULLY INTEGRATED
COAL LIQUEFACTION/CHARACTERIZATION TECHNIQUES**

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INTRODUCTION

Over the past decade, sophisticated chromatographic and spectroscopic techniques have greatly increased our knowledge of the composition and structure of coal-derived liquids as well as of the corresponding feed coals [1]. Notwithstanding these advances, relatively little is known about the precise reaction pathways as well as the intermediate reaction products involved. In order to study these processes in greater detail, previous activities in our laboratory have focused on the development of advanced mass spectrometric techniques in which thermally driven coal conversion reactions are carried out directly within the vacuum environment of an MS ion source (e.g., vacuum TG/MS [2], Curie-point Py-MS [3]) or at near-ambient pressures with a capillary transfer line connection to a combined IR/MS system (e.g., TG/(GC)/IR/MS [4]) while maintaining sufficiently short sampling intervals to provide kinetic information. Although successful in modeling and even predicting [5], a range of different coal liquefaction, devolatilization and gasification reactions, an inherent shortcoming of this class of techniques is the inability to simulate catalytic coal conversion processes at high pressures. Consequently, we have undertaken the development of a direct MS interface for high pressure reaction products under real-time analysis conditions while minimally disturbing the reaction process.

Effectively, whereas our earlier work attempted to bring the reactor into the mass spectrometer, we are now making an effort to bring the mass spectrometer into the reactor. Beside providing us with the opportunity to study coal conversion processes under more realistic reaction conditions, the new approach also enables us to interface our spectrometric equipment to a broader range of existing reactor types and processing environments. In doing

so, we were fortunate enough to profit from several recent developments with regard to automated vapor sampling techniques for GC/MS [6] as well as with regard to mobile, ruggedized GC/MS instruments [7] suitable for use in a wide variety of demanding industrial process engineering environments.

EXPERIMENTAL

A high priority objective in our present work is development of on-line GC/MS monitoring techniques for batch or flow through type autoclave reactors. Due to the relatively long residence times primary reaction products formed in autoclaves are notoriously susceptible to secondary, or even tertiary reactions. Application of real-time, on-line chromatographic and/or spectroscopic techniques capable of throwing light on these processes is hampered by the high temperatures and pressures inside the reactor which complicate direct interfacing to standard analytical instruments.

Using a novel automated vapor sampling (AVS) technique developed at the University of Utah, Center for Micro Analysis and Reaction Chemistry (U.S. Patent No. 4,970,905), we constructed an on-line mass spectrometry interface for high pressure reactor environments (see Figure 1. The interface consists of a valveless, all quartz, heated inlet device suitable for automated, repetitive vapor sampling. The AVS module connects directly to a 1 m long, 150 μm i.d., fused silica capillary GC column, thereby providing a highly useful degree of chromatographic pre-separation. The effluent from the capillary column is fed directly into the ion source of a highly sensitive ion trap mass spectrometer (ITMS) capable of operating in GC/MS as well as tandem MS (MS^n) mode while providing electron ionization (EI) as well as chemical ionization (CI) options.

Since the AVS inlet is designed to operate at near-ambient pressures in order to ensure a constant, stable flow of carrier gas through the capillary transfer line column into the high vacuum of the MS system, the high pressures in the autoclave reactor need to be first reduced to near-ambient pressure by means of a 1 m length of narrow bore (e.g. 10 μm) fused silica capillary tubing. This tubing is kept at relatively high temperatures ($< 300\text{ C}$) to minimize condensation losses. Moreover, utmost care is taken to eliminate dead spaces at the high pressure end of the transfer line in order to avoid undue long response times due to the very low liquid flows (e.g. $\sim 0.1\ \mu\text{l}/\text{min}$) in the narrow bore capillary tube.

Figure 1 shows a schematic picture of the on-line system, whereas Tables 1 and 2 list the experimental conditions for a series of on-line GC/MS studies with model compounds, aimed at establishing the feasibility of our instrumental approach. A second objective was to perform preliminary studies of low temperature hydrotreatment and hydro-de(oxygen)(nitrogen)(sulfurization) processes playing a key role in ongoing low temperature coal liquefaction studies under the University of Utah task within the Consortium for Fossil Fuel Liquefaction Science.

RESULTS AND DISCUSSION

Aside from occasional plugging of the 10-15 μm i.d. capillary pressure reduction line and the protective 2 and 0.5 μm frits the system performed reliably. The cause of the plugging appears to be traceable to particles released by the catalyst. Obviously, more sophisticated particulate matter removal strategies are needed before on-line analysis of conversion processes in coal solids can be attempted. Consequently, current experimental

protocols call for the analysis of carefully filtered liquid samples ranging from model compounds to actual coal derived liquids and/or subfractions.

Apart from these limitations, system performance exceeded design specifications with regard to GC/MS performance, especially isothermal GC resolution (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 concentrations thus establishing an effective dynamic range $\geq 10^4$). As also demonstrated in previous work [8], 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 the typical reaction times in autoclave reactors.

Specific results of the three series of experiments shown in Figures 2-7 illustrate the ease with which kinetic profiles of reactor feed as well as reaction products can be obtained in a single experimental run. Using conventional off-line experiments, which usually require the experiment to be repeated numerous times while increasing temperature and/or residence time, it would have taken several weeks or months to obtain equally detailed kinetic profiles, as many among us know all too well from personal experience with autoclave type experiments. It should also be noted that the reduction in number of experiments carried out greatly lessens the demand for excessive quantities of expensive model compounds as well as the eventual disposal of hazardous experimental wastes. Finally, the ability to measure both

the feed components and the reaction products in a single experiment should be instrumental in helping to close mass balances as well as elucidate reaction pathways. The mild hydrocracking (Figures 2 and 3), hydrodeoxygenation (Figures 4 and 5) and hydrodenitrogenation and -desulfurization (Figures 6 and 7) experiments provide readily interpretable information about the mechanisms and the kinetics of the primary conversion reactions under catalytically as well as thermally controlled reaction conditions.

CONCLUSIONS

1. Aside from occasional plugging of the capillary pressure reduction line, the system performed reliably and according to design specifications.
2. Valveless, pulsed sampling of reactor effluents onto short capillary GC columns provides complete GC/MS profiles at 1-4 min intervals. For nonretained sample components the transfer time between reactor and detector is less than 1 minute.
3. A highly useful degree of chromatographic pre-separation is achieved as evidenced by the separation of the two decalin (cis and trans) isomer peaks.
4. Use of stable solvents in a 9:1 solvent/feed ratio does not adversely affect the performance of the chromatographic system, even if the solvent peak elutes later than most of the reaction product peaks.
5. Product concentrations of less than 100 ppm are readily monitored under the same GC/MS conditions as the solvent peak, thereby establishing an effective dynamic range $\geq 10^4 : 1$.

6. Effects of time, temperature and catalyst type on hydrocracking and hydrode(oxygen)(nitrogen)(sulfuriz)ation are readily measurable.
7. Kinetic profiles of feed as well as product concentrations can be obtained in a fraction of the time needed for conventional off-line measurements.

FUTURE PLANS

To obtain precise mass balance information we are planning to perform similar on-line GC/MS experiments on catalytic and thermal coal conversion reactions in a high pressure TG System. Also, this will further reduce the feed sample quantities needed per experiment, thereby permitting the use of rare and/or expensive model compounds. Since high pressure TG/MS experiments will need to be primarily carried out in solventless environments (e.g. under hydrolysis conditons) particulate matter related plugging problems (frits and transfer lines) should be eliminated.

Up till now only relatively simple model compound mixtures have been studied. Nevertheless, the system is expected to perform quite well with more complex samples such as actual coal-derived liquids. In spite of the rather limited range of compounds which can be analyzed in a single isothermal GC run the formidable analytical capabilities of the ion trap mass spectrometer used in these experiments, which include tandem MS (MS^n), as well as various chemical ionizations options, compensate for the shortcomings of the GC system in many applications. Furthermore, we are currently equipping the transfer line GC module with rapid temperature programming (up to 10 K/sec) capability. This should considerably extend

the range of compounds which can be analyzed in a single GC/MS run, albeit at the expense of longer repetitive intervals, due to the time needed to cool the transfer line between runs.

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TABLE I

| Reaction Type | Feed | Solvent | Internal Standard | Products | Temp. | Catalyst |
|-------------------|---|----------------------|-------------------|--|-------|---|
| HT | diphenyl methane | decalin | biphenyl | benzene toluene | 350 C | none |
| HT | diphenyl methane | decalin | biphenyl | benzene toluene | 350 C | FeCl ₃ / SiO ₂ - Al ₂ O ₃ |
| HDO | dibenzyl ether | decalin | biphenyl | toluene xylenes | 340 C | none |
| HDO | dibenzyl ether | decalin | biphenyl | toluene xylenes | 300 C | CoMo/ γ - Al ₂ O ₃ |
| HDN, HDS & HDO | indole diphenyl sulfide diphenyl ether | trimethyl benzene | dodecane | benzene 4-amino- benzonitrile 2-ethyl- benzenamin c | 300 C | CoMo/ γ - Al ₂ O ₃ |

TABLE II

| | |
|-------------------------------------|---|
| Reactor Conditions: | |
| - Reactor | Autoclave Engineering, Inc. (Penn.) |
| - Reactor Volume | 50 cc |
| - Pressure | 1600-1650 psi |
| - Feed Flow Rate | 30 cc/hr |
| - Reaction Gas | continuous flow H ₂ 50 sccm |
| - Heating Speed | ambient --> 300 C in ~18 min |
| - Final Reaction Temperature | thermal reaction 340 C, catalytic reaction 300 C |
| - Catalyst | ~1 g sulfonated COMO/r-Al ₂ O ₃ |
| Pressure Reduction Line Conditions: | |
| - Pressure Reduction Line | 1 m x 10-15 um i.d. fused silica capillary tube |
| - Temperature | 175 C |
| - Pressure | 1600-1650 psi --> ambient pressure |
| - Liquid Flow | ~0.1 ml/min |
| Sample Inlet Conditions: | |
| - Temperature | 270 C |
| - Pressure | ambient pressure |
| - 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 for dibenzyl ether 550 ms at 3 min intervals for model compound mixtures |
| Transfer Line Conditions: | |
| - Column | 1 m x 150 um i.d. coated with 0.12 um CP-SIL 5CB |
| - Temperature | dibenzyl ether reaction 105 C model compound mixture reaction 80 C |
| - Pressure | ambient --> 10 ⁻⁶ torr |
| MS Conditions: | |
| - Mass Spectrometer | Finnigan MAT Ion Trap MS |
| - Pressure | 10 ⁻⁶ torr |
| - Ion Trap Temperature | 96 C |
| - Ionization | electron impact (with automatic gain control) |
| - Spectrum Scanning Speed | 4 spectra/s |
| - Mass Range | m/z 50-200 |

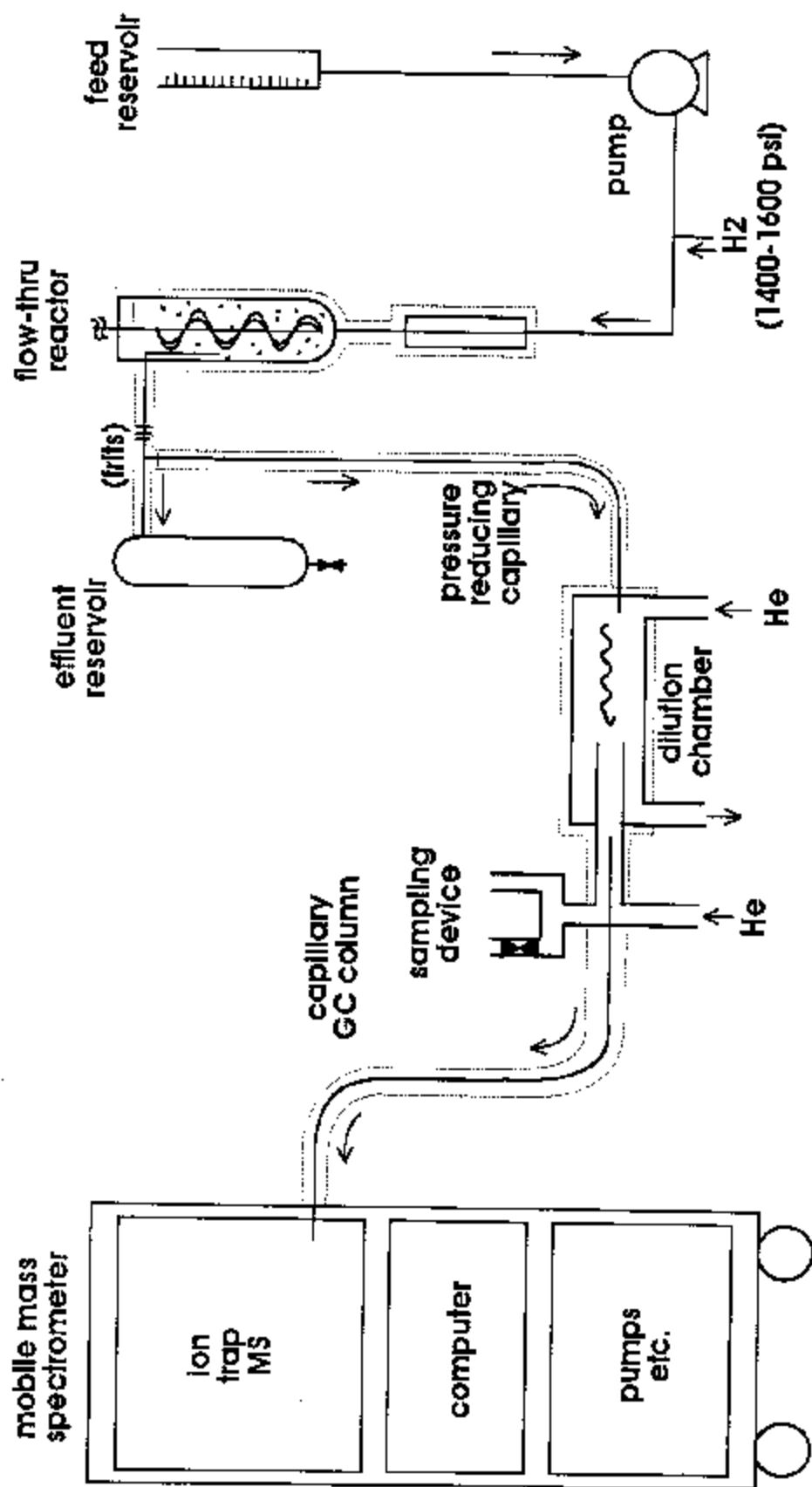


Figure 1. On-line GC/MS monitoring of high pressure reactor.

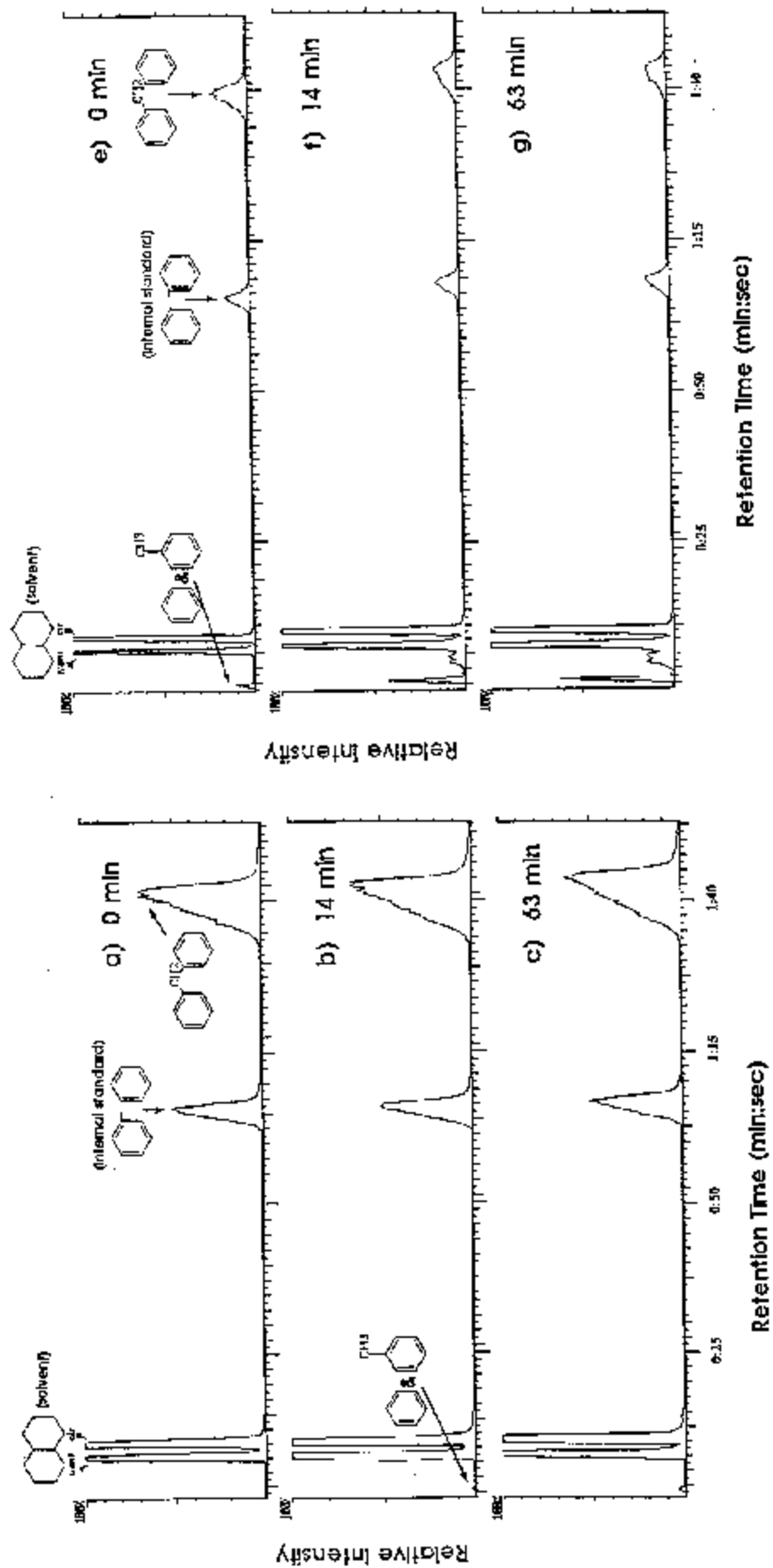


Figure 2. Total ion chromatogram profiles obtained at 350 C, for different reaction times of diphenyl methane under thermally (a-c) and catalytically (d-f) controlled hydrotreatment conditions. Note GC separation of decaalin solvent isomers.

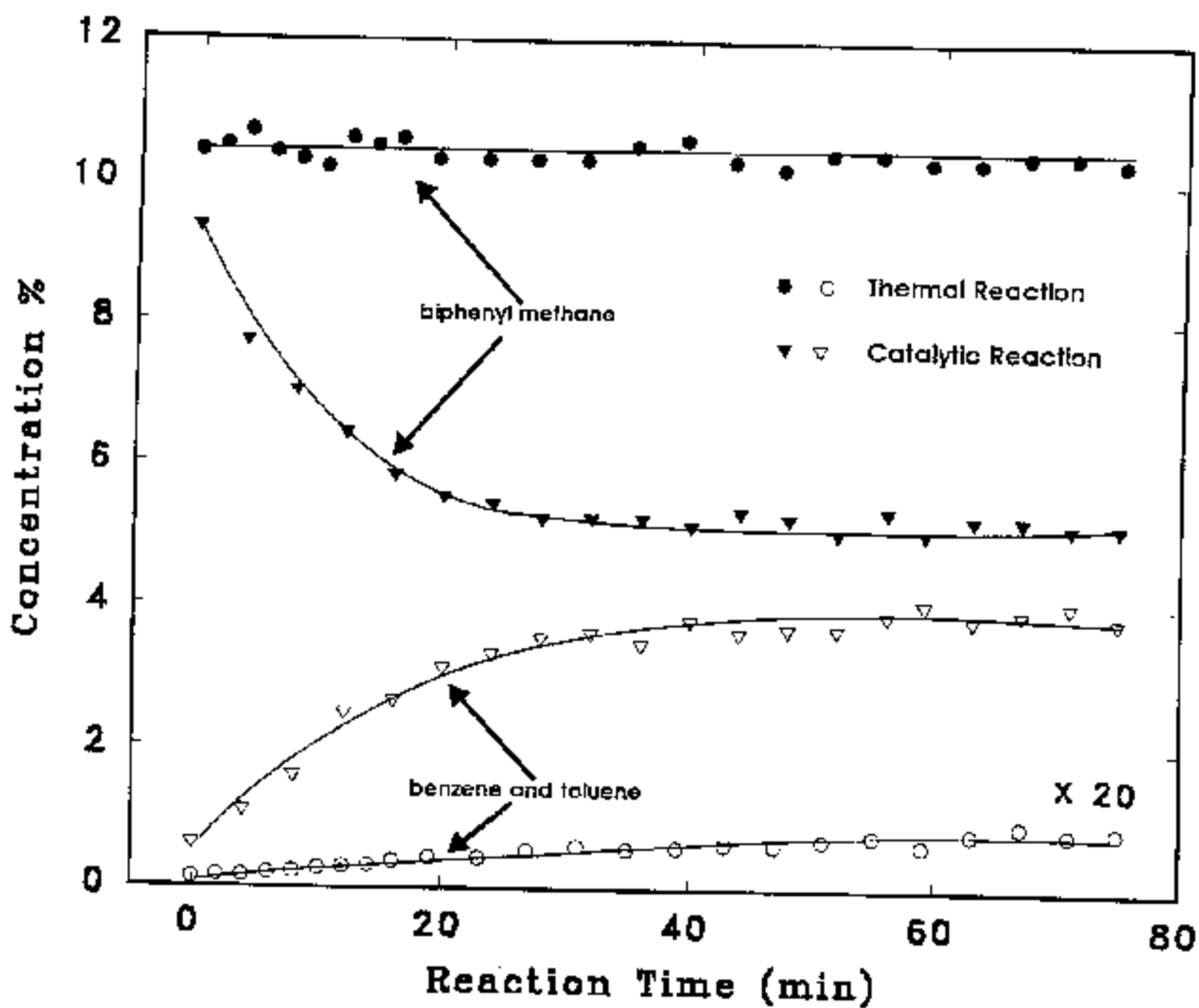


Figure 3. Kinetic profiles of diphenylmethane conversion (●, ▼) and benzene and toluene formation (○, ▽) under thermally (●, ○) and catalytically (▼, ▽) controlled conditions. Note major increase in reaction rate in the presence of catalyst.

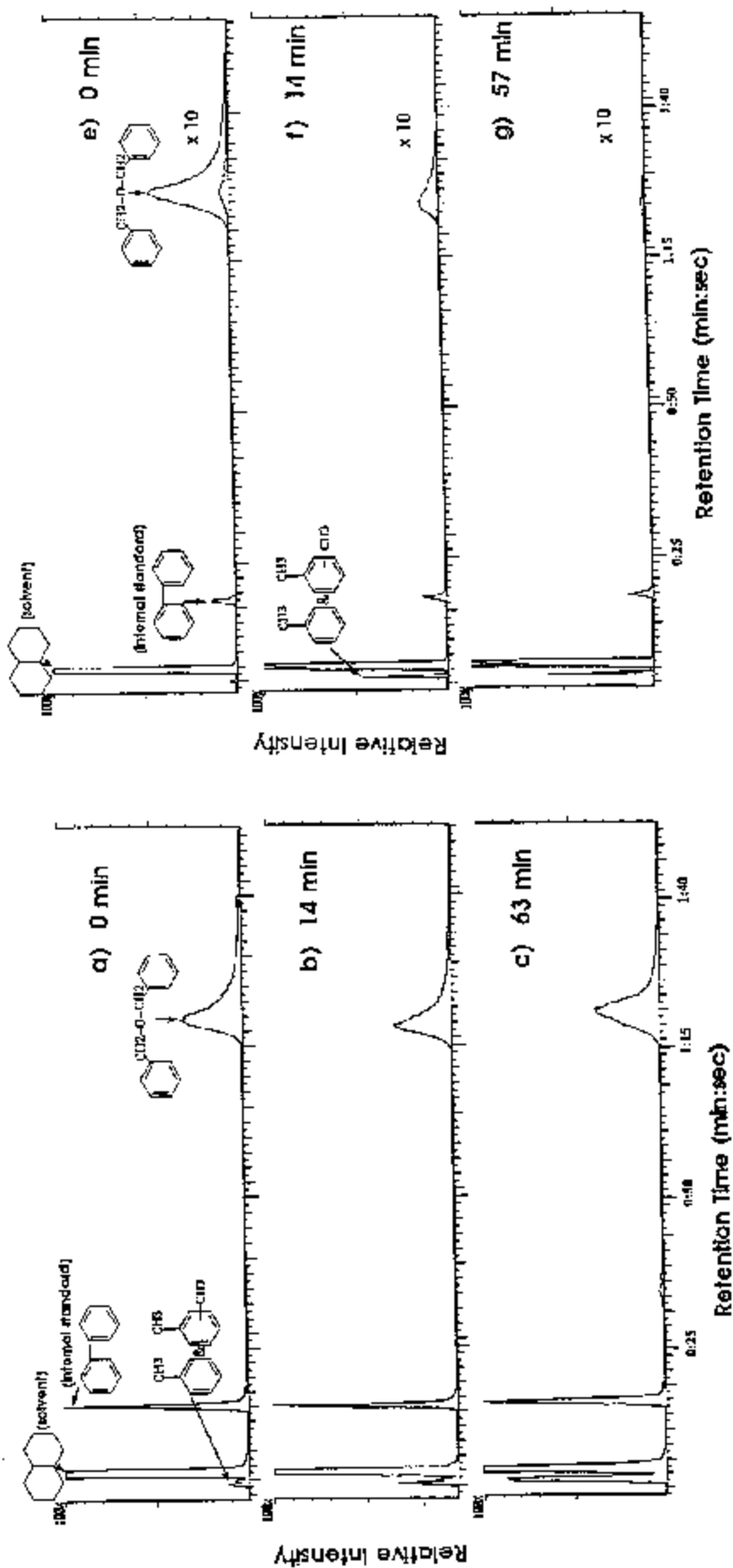


Figure 4. Total ion chromatogram profiles obtained at 340 C and, 300 C for different reaction times of dibenzyl ether under thermally (a-c) and catalytically (d-f) controlled hydrodeoxygenation conditions, respectively.

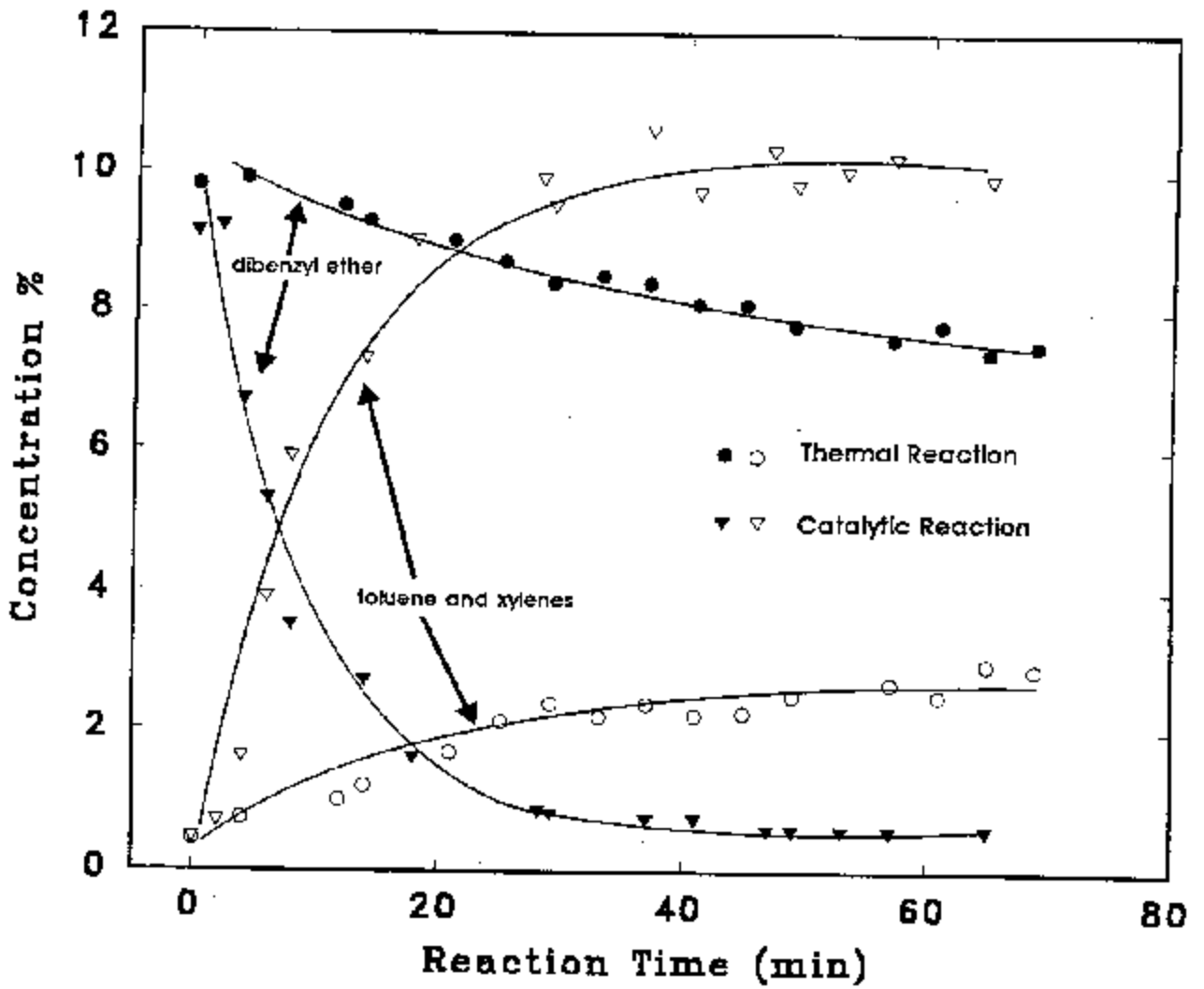


Figure 5. Kinetic profiles of dibenzylether conversion (●, ▼) and toluene and xylenes formation (○, ▽) under thermally (●, ○) and catalytically (▼, ▽) controlled conditions.

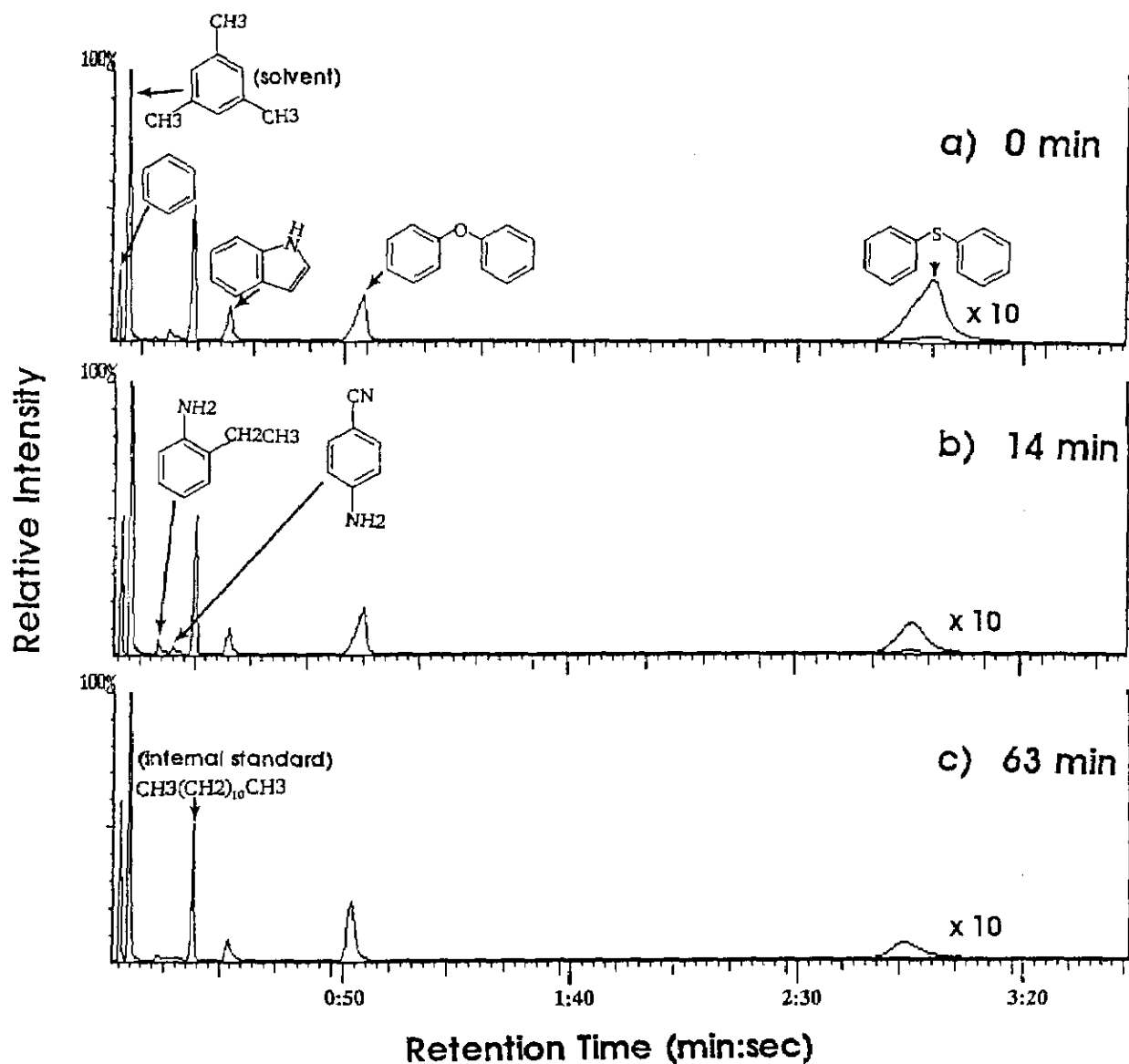


Figure 6. Total ion chromatogram profile obtained at 300 C, for different reaction times of diphenyl ether, indole and diphenyl sulfide under catalytically controlled hydrode(oxygen)(nitrogen)(sulfurization) conditions.

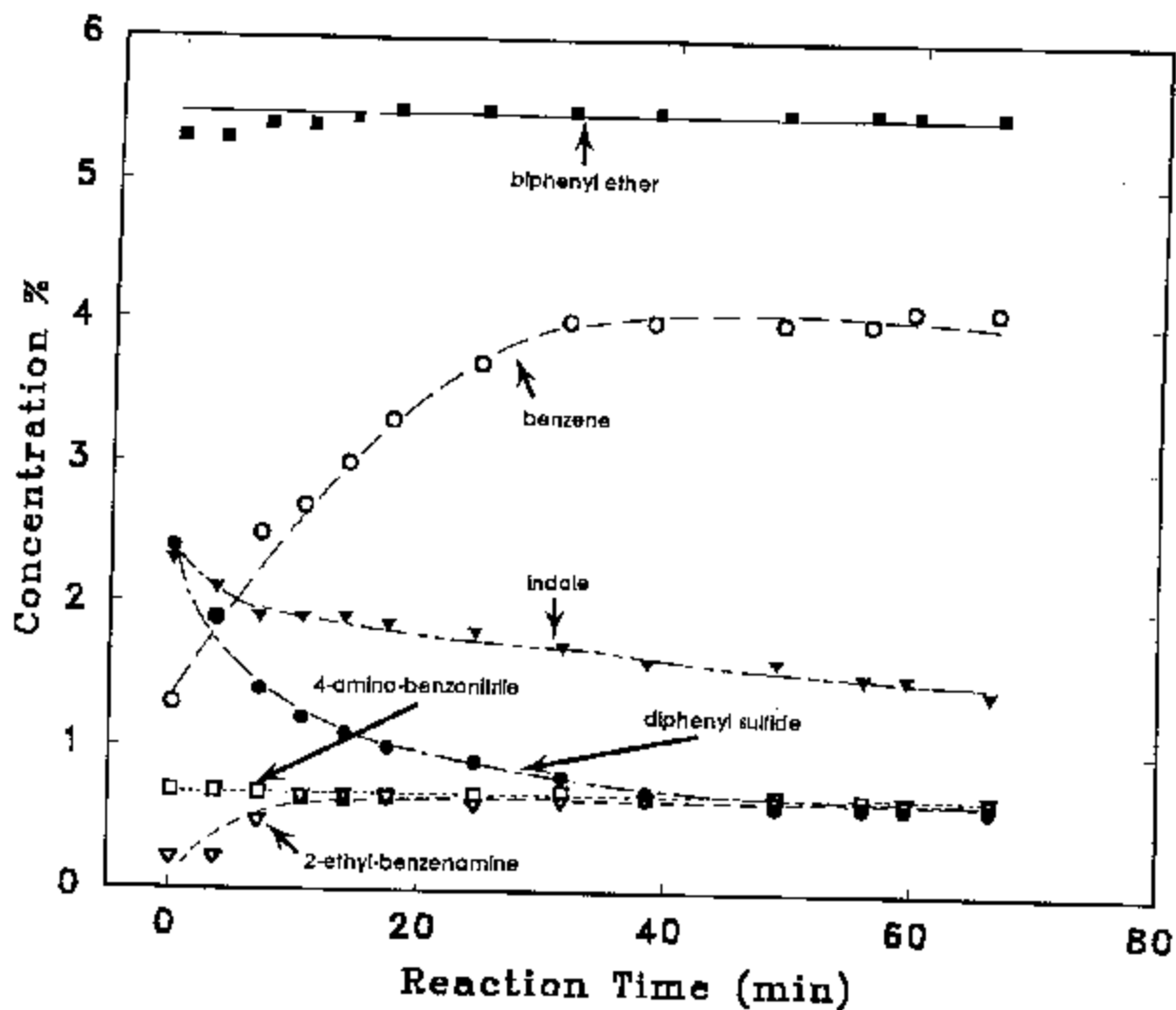


Figure 7. Kinetic profiles of diphenyl ether, indole and diphenyl sulfide conversion ($\blacksquare, \blacktriangledown, \bullet$) as well as benzene, 2-ethyl-benzenamine and 4-amino-benzonitrile formation (\circ, ∇, \square) under catalytically controlled conditions.