# STUDIES OF DEACTIVATING SPECIES ON COAL LIQUEFACTION CATALYSTS*

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## INTRODUCTION

Previous studies (1,2) of catalyst samples from laboratory experiments with model compounds and coal-derived hydrotreater feeds from the Wilsonville Advanced Coal Liquefaction R&D Facility have shown that most deactivation is due to hydrotreating strongly basic heterocyclic nitrogen compounds. For example, hydrotreating nitrogen polycyclic aromatic compounds, separated from a hydrotreater feed from Wilsonville run 247, caused a 95% loss of the catalyst's hydrogenation (HYD) activity within a 2 h run. This activity loss was much greater than obtained by hydrotreating the whole hydrotreater feed or the other chemical classes of compounds (aliphatics, neutral polycyclic aromatic compounds, hydroxy polycyclic aromatic hydrocarbons) that made up the feed. Hydrotreating model compounds representative of the different types of nitrogen compounds present in coal liquids, including strongly basic compounds (quinoline, pyridine, acridine), a weakly basic compound (indole), and a neutral compound (carbazole), showed that the strongly basic compounds caused greater deactivation than the other compounds. Losses of about 75% of the HYD activity were observed by hydrotreating the strongly basic compounds in 2 h reactions, compared with a 50% loss for indole and a 24% loss for carbazole.

Quinoline hydrotreating studies (3) were performed to determine the effects of process conditions on deactivation caused by hydrotreating strongly basic nitrogen compounds. The reactions were carried out at two times (5 min, 2 h) and two temperatures (300°C, 400°C). The results showed that the deactivation was the same in all cases. Gas chromatographic (GC) analyses of the liquid products from these runs demonstrated that increasing reaction severity yielded more unidentified compounds (i.e., compounds that were not part of the reported quinoline hydrodenitrogenation (HDN) reaction scheme (4)). At the lowest reaction severity condition (300°C, 5 min), 19% of the liquid product consisted of unidentified compounds, whereas at the highest severity condition (400°C, 120 min) 86% was unidentified. At low severity, only 2% of the nitrogen was removed, as determined by liquid product analyses, whereas at high severity 18% was removed. A comparison of the amount of nitrogen remaining in the liquid product from the high severity reaction with gas chromatographic analyses of the liquid product showed that most of the remaining nitrogen was present in compounds that were formed by side reactions.

The ultimate objectives of the catalyst deactivation work reported here are to determine how the deactivation due to hydrotreating strongly basic nitrogen compounds occurs on the catalyst surface and to identify the compounds that cause the deactivation. The work reported here is aimed at evaluating the usefulness of Field Ionization Mass Spectrometry (FIMS) analyses for our catalyst deactivation studies. Results of the application of FIMS techniques to characterize the compounds volatilized from the aged catalysts and the liquid

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products of our quinoline HDN experiments are described. The results are compared to those obtained for catalysts used at Wilsonville. The field emission method employed in FIMS is a mild, yet efficient, ionization that exclusively produces molecular ions from most chemical compounds. Thus the mass spectra of complex mixtures are not complicated by the presence of large numbers of peaks associated with molecular fragments. FIMS thus provides molecular profiles of samples. It has been used in the characterization of both petroleum and coal derived-materials (5-7). The relative ionization efficiencies of many different classes of organic compounds analyzed by FIMS are very similar, varying by only a factor of two (8).

## EXPERIMENTAL PROCEDURES

FIMS results are reported for aged catalysts from Wilsonville runs 246 and 247 and for catalysts and products from quinoline hydrotreating experiments (3).

### Materials

The catalyst used both for processing coal at Wilsonville and for the laboratory hydrotreating experiments was Shell 324M, which contains 12.4 wt% Mo and 2.8 wt% Ni on an alumina support, in the form of extrudates measuring about 0.8 mm in diameter and 4 mm in length. Prior to use in the laboratory experiments, the catalyst was presulfided with a 10 mol% $H_2S/H_2$ mixture at 400°C and atmospheric pressure for 2 h. Before analysis, all aged catalyst samples were Soxhlet extracted with tetrahydrofuran, to remove as much soluble material as possible, and then dried overnight at 100°C under vacuum.

### Wilsonville Catalysts

Two catalyst samples from each of two Wilsonville runs were analyzed by FIMS. The run 246 samples had catalyst ages of 36 and 592 lb resid/lb catalyst and the run 247 catalysts had ages of 28 and 546 lb resid/lb catalyst. Catalyst age was determined from the amount of resid, which is nondistillable material at 600°F and 0.1 mm Hg, in the Wilsonville hydrotreater feed. Activity test results and characterization results of these Wilsonville samples have been reported previously (9).

Run 246 processed subbituminous Wyodak coal using the Double-Integrated Two-Stage Liquefaction (DITSL) mode up to a catalyst age of about 300 lb resid/lb catalyst and the Integrated Two-Stage Liquefaction (ITSL) mode for the remainder of the run. Deashing was performed between the two stages. In the DITSL mode, only the light thermal resid from the deasher went to the hydrotreater, whereas in the ITSL mode all the deashed material went to the hydrotreater. The temperatures in this run ranged from about 320°C to 340°C.

Run 247 processed Illinois #6 coal in the Reconfigured Integrated Two-Stage Liquefaction mode. In this mode, the deashing occurs after the second stage so that all the material from the first stage goes to the hydrotreater. The run temperatures ranged from 350°C to 375°C.

### Quinoline Hydrotreating Experiments

Each hydrotreating experiment was performed in a 26 cc batch microreactor with 1200 psig $H_2$ cold charge pressure. Runs were made for either 5 minutes or 2 hours at either 300°C or 400°C. Experiments were performed with 1.5 g of model compound and 0.5 g presulfided catalyst. Activity test results and characterization results for the aged catalysts from these reactions have been reported previously (3).

### FIMS Analysis

FIMS uses a field emission device to ionize the constituents of the vapor

released from a sample when it is heated in an evacuated chamber. The ions are separated by mass in a magnetic sector mass spectrometer. The field ionization mass spectrometer at SRI International, which was used in this study, consists of an activated tantalum foil field source interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and analysis. A single catalyst pellet or about 50 mg of liquid product was placed in a sample holder and introduced into the mass spectrometer through a heatable direct-insertion probe. Spectra were collected by scanning the spectrometer repeatedly over the 50 to 800 amu range while the sample was gradually heated. The heating range for the catalyst samples was about 25°C to 450°C, whereas the liquid products were heated from about -60°C to 350°C.

## RESULTS

### Wilsonville Catalysts

Results of the FIMS analyses on the run 246 catalysts (Figure 1 and Table 1) show that the average molecular weights of the volatile species increase with catalyst age; the weight average molecular weight increases from 256 to 278. In addition, the number of peaks increases from 382 to 465 with age. Analyses of the molecular weights show that at least 49% of the peaks are due to nitrogen compounds; compounds with an odd number of nitrogen atoms have odd numbered molecular weights (10). Although there are approximately an equal number of odd and even mass peaks, 60% of the total ion intensity is present in the odd molecular weight peaks. The nine highest intensity peaks from the 36 lb resid/lb catalyst sample and 16 out of the highest 24 peaks are due to nitrogen compounds. In the higher aged catalyst, the highest 14 peaks and 22 out of the highest 24 peaks are due to nitrogen containing compounds.

The FIMS analyses of the two catalyst samples from run 247 (Figure 2 and Table 1) show similar trends to those observed for the run 246 catalysts. The weight average molecular weights increase with catalyst age. The increases are about 24% for these catalysts as compared to about 8% for the run 246 catalysts. About 48% of the peaks in the spectra from the run 247 samples have odd numbered molecular weights. The total number of peaks also increases with catalyst age. About 52% of the total ion intensity in the 28 lb resid/lb catalyst sample and 47% in the 546 lb resid/lb catalyst sample are due to nitrogen compounds. For the 28 lb resid/lb catalyst sample, the highest 6 peaks and 18 out of the highest 24 peaks are due to nitrogen compounds. The higher aged sample from run 247 had 13 nitrogen compounds out of the 24 compounds with the highest peaks.

There is also evidence for the presence of many alkylated compounds in all four of the Wilsonville catalyst spectra. For example, in the 36 lb resid/lb catalyst sample, each peak in the series 216, 230, 244, 258, 272, 286, 300 and 314 differs from the next peak by 14 mass units suggesting that the compounds yielding these spectra differ by one $CH_2$ group. This series is also present in the other three spectra, although the number of compounds in the series and the intensities of the peaks vary. In addition, there are many other series, with peaks differing by 14 mass units, that suggest the presence of additional alkylated compounds.

### Catalysts from Quinoline Experiments

Results of the FIMS analyses on the catalysts from the quinoline hydrotreating experiments (Figure 3 and Table 1) show that the number of peaks obtained increases with both reaction time and temperature. The volatile material from the catalyst used in the 300°C 5 minute reaction has an average molecular weight comparable to that of quinoline (129), although FIMS spectra of

the volatile material from all the other catalysts have higher average molecular weights than either quinoline or the highest molecular weight compound reported in the quinoline HDN reaction scheme (4) (propylcyclohexylamine, 141). The spectrum for the volatile material from the catalyst from the 300°C 5 minute reaction shows that about 68% of the total ion intensity is due to quinoline. The spectrum of the catalyst from the 300°C 120 minute reaction also shows quinoline as a major peak, but has an additional major peak with a molecular weight of 202. The compound causing this peak and the origin of this compound are unknown. The catalysts from the two 400°C reactions each have the same major peaks, although the intensities are different. The only identifiable peak, based on the quinoline HDN reaction scheme, out of the highest 8 peaks in these patterns is that due to quinoline.

**Liquid Products from Quinoline Experiments**

The spectra obtained from the liquid products (Figure 4) from the quinoline HDN reactions are very different from those obtained from the catalysts. There are many more peaks present in the product spectra than in the spectra of the material volatilized from the catalyst; about half of the peaks in each product spectrum are due to nitrogen compounds. The average molecular weights of the products are also much higher than for the volatile species from the catalyst samples. The spectrum of the product from the 300°C 5 minute reaction has one major peak with a molecular weight of 133 that makes up about 64% of the total ion intensity. This peak is due to tetrahydroquinoline (THQ), 1,2,3,4- THQ, 5,6,7,8-THQ or both. This spectrum is different than that obtained from the catalyst used in this reaction, which had quinoline as the major peak and only a very small amount of THQ. The spectrum from the 300°C 120 minute reaction product also has 133 as the highest peak, but in addition it has a significant peak at 266 and a peak at 399 indicating the presence of THQ dimers and trimers. There is a small peak at 135, which is the molecular weight of o-propylaniline (OPA). The spectrum of the product from the 400°C 5 minute reaction also shows the presence of THQ as the major peak and a peak due to the THQ dimer. There's a larger quinoline peak in this pattern than observed in the 300°C product spectra; this is reasonable since hydrogenation occurs more readily at the lower temperature. The product spectrum from the 400°C 120 minute reaction has 624 peaks with at least 70% of the total ion intensity due to nitrogen compounds. The highest intensity peak in this pattern is at a mass of 135, which is probably due primarily to OPA. There is also evidence in this spectrum of the presence of alkylated species. The series of peaks 129, 143, 157, 171 and 185 indicate the presence of alkylated quinoline compounds. The series 93, 107, 121, 135, 149 and 163 also suggests the presence of alkylated species.

## DISCUSSION

The results of the FIMS analyses of the Wilsonville catalysts indicate that some nitrogen compounds are preferentially adsorbed on the catalyst. An analysis of a hydrotreater feed from run 247 (11) has shown that the maximum amount of nitrogen compounds in the hydrotreater feed would be approximately 17%, whereas about 50% of the compounds volatilized from the catalysts are nitrogen compounds. This preferential adsorption of nitrogen compounds is not surprising since many nitrogen compounds are basic compounds that would be readily adsorbed on acidic catalyst sites. These results do suggest, in agreement with previous studies (1,2), that nitrogen compounds are the precursors of the compounds responsible for catalyst deactivation. The increase in the average molecular weights of the volatile compounds with catalyst age could be due to several factors: retrogressive reactions occurring on the catalyst surface (due to either time at temperature in the Wilsonville run or

the desorption procedure in the FIMS analyses), or changes in the hydrotreater feed as the run progresses. Hydrotreater feeds, withdrawn from the pilot plant at the same times as the catalyst withdrawals, were not available for FIMS analyses.

Analyses of spectra taken of catalysts from HDN reactions with quinoline are a little easier to interpret than spectra of Wilsonville catalysts because the reactor feed is known and the HDN reaction scheme has been reported (4). Therefore, it is possible to identify some of the peaks in the FIMS spectra and to ascertain which expected peaks are not present.

Results of studies of the Wilsonville catalysts and the quinoline hydrotreating catalysts suggest that FIMS is a very useful technique for helping identify compounds adsorbed on catalysts during reaction. Based on the results of these studies, we have identified several blank and baseline analyses that should be performed in order to elucidate the significance of the analyzed compounds in regard to either studying reaction mechanisms or determining deactivation mechanisms. First, quinoline and several other compounds that are part of the HDN reaction scheme should be adsorbed on the catalyst at room temperature and the samples then analyzed by FIMS to determine if other compounds are formed catalytically in the desorption step of the analysis. Although changes in compounds have not been found to be a problem with liquid samples, this could be a problem on a catalyst surface when high temperatures are present. Second, analyses should be performed on ground -200 mesh catalysts so that diffusional limitations in the catalyst are minimized. Identification of individual compounds in the FIMS spectra is imprecise because of the limited information available for each peak. Attempts to correlate volatilization temperature to compound properties (such as adsorption energy) have not been effective with catalyst samples because of the wide temperature range over which each compound is volatilized. This could be related to the catalyst's effective diffusivity in addition to the compounds properties. If diffusional limitations are minimized, compounds should be volatilized over a smaller temperature range than occurs with extrudates. The volatilization temperature might then be useful in helping identify the compound. Third, FIMS analyses should be repeated on several catalyst pellets from a given hydrotreating reaction. This would not only indicate the reproducibility of the analysis of catalysts, but would also give sufficient catalyst for both elemental analyses (so that the amount of volatile material could be determined) and activity testing (so that the impact of the volatile material on activity could be evaluated). Finally, catalyst samples and hydrotreater feeds removed from the Wilsonville facility at the same time should be analyzed to determine interactions between the feed and catalyst.

The results of the analyses of the liquid products provide information about the effects of reaction conditions on the product. The liquids are completely volatilized in the FIMS analyses so that all compounds are analyzed. In addition, results of the FIMS analyses have been compared to previous quantitative GC analyses of the liquid products from these hydrotreating reactions. For the product from the 300°C 5 minute reaction, GC analysis gave about 5 wt% quinoline, 76 wt% THQ, and 19 wt% unknown compounds (i.e. compounds that are not part of the HDN reaction scheme), and FIMS gave 3 % quinoline, 70 % THQ, and 27 % unknown compounds. The results of these two analyses are in good agreement; the agreement between the GC and FIMS analyses of the liquid products from the other three reactions at the more severe reaction conditions were equally good. These results indicate, in agreement with previous studies, that there are no chemical changes in the samples due to the FIMS analysis. FIMS analysis gives additional information about the compounds that cannot be obtained with GC alone.

## CONCLUSIONS

The results of this study indicate that FIMS analyses are useful for characterizing changes that occur in the feed during hydrotreating. Potential changes that can be quantified include molecular weight distributions, number of compounds and types of compounds. If FIMS analyses are combined with other analytical techniques such as Fourier transform infrared spectroscopy and GC/mass spectrometry, it should be possible to identify many of the compounds in the reaction products. Results of studies of the compounds volatilized from aged catalysts also suggest that FIMS is potentially useful for determining catalytic reaction mechanisms and for studying catalyst deactivation. Additional experiments are being carried out to clarify the interpretation of these results.

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Table 1. FIMS data for the catalyst and product samples

**Wilsonville Catalysts**

| | Catalyst Age | Wt Av MW* | % Odd MW Intensity | Number of Peaks | % Odd MW Peaks |
|---|---|---|---|---|---|
| Run 246 | 36 | 255.7 | 59.5 | 382 | 48.9 |
| | 592 | 277.5 | 60.2 | 465 | 49.2 |
| Run 247 | 28 | 247.5 | 51.9 | 401 | 48.4 |
| | 546 | 304.4 | 46.5 | 424 | 46.7 |

**Quinoline HDN Catalysts**

| Reaction Conditions | Wt Av MW | % Odd MW Intensity | Number of Peaks | % Odd MW Peaks |
|---|---|---|---|---|
| 300°C, 5 min | 131.5 | 81.2 | 41 | 51.2 |
| 300°C, 120 min | 173.6 | 48.7 | 60 | 40.0 |
| 400°C, 5 min | 174.0 | 52.4 | 146 | 34.2 |
| 400°C, 120 min | 166.7 | 52.2 | 343 | 45.8 |

**Quinoline HDN Product**

| Reaction Conditions | Wt Av MW | % Odd MW Intensity | Number of Peaks | % Odd MW Peaks |
|---|---|---|---|---|
| 300°C, 5 min | 201.9 | 75.8 | 182 | 55.5 |
| 300°C, 120 min | 275.6 | 55.6 | 344 | 52.2 |
| 400°C, 5 min | 287.7 | 59.2 | 560 | 49.7 |
| 400°C, 120 min | 295.2 | 70.3 | 624 | 50.0 |

* Average molecular weight

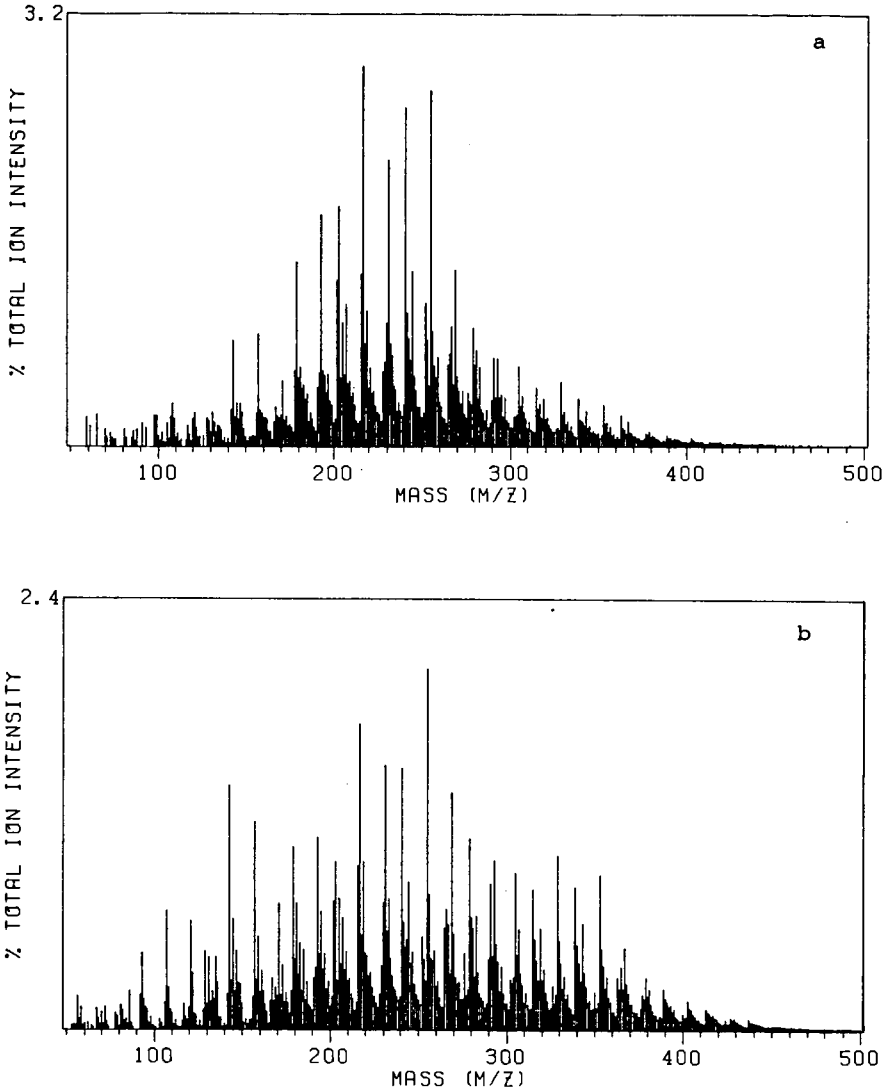
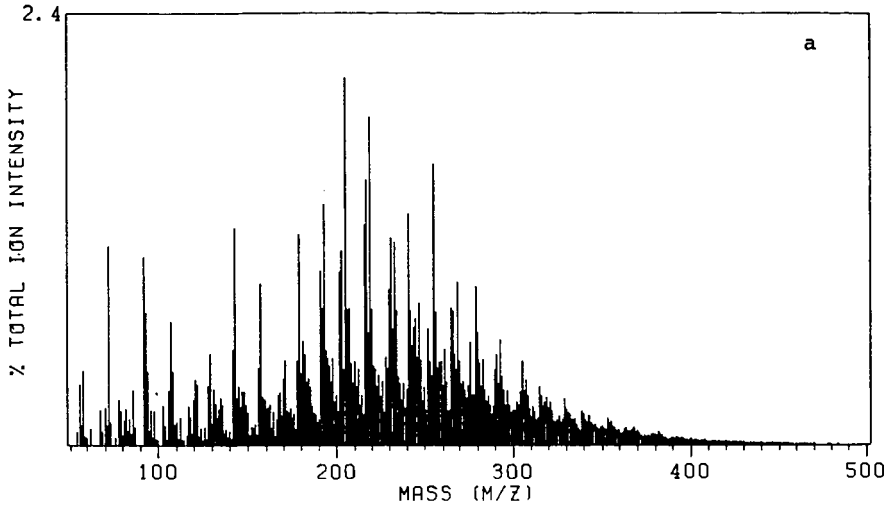



Figure 1. FIMS spectra of Wilsonville run 246 catalysts.
a = Catalyst age of 36 lb resid/lb catalyst;
b = Catalyst age of 592 lb resid/lb catalyst.



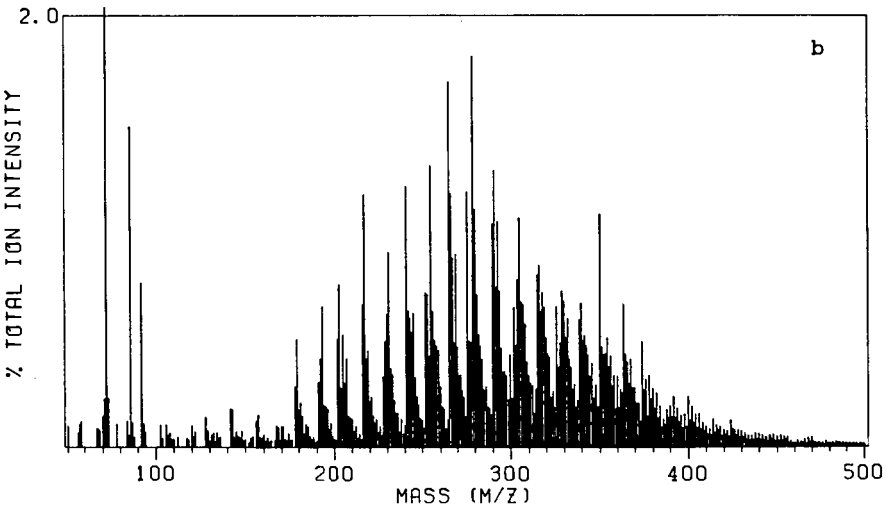




**Figure 2.** FIMS spectra of Wilsonville run 247 catalysts.
a = Catalyst age of 28 lb resid/lb catalyst.
b = 546 lb resid/lb catalyst.

Figure 3. FIMS spectra of quinoline HDN catalysts.

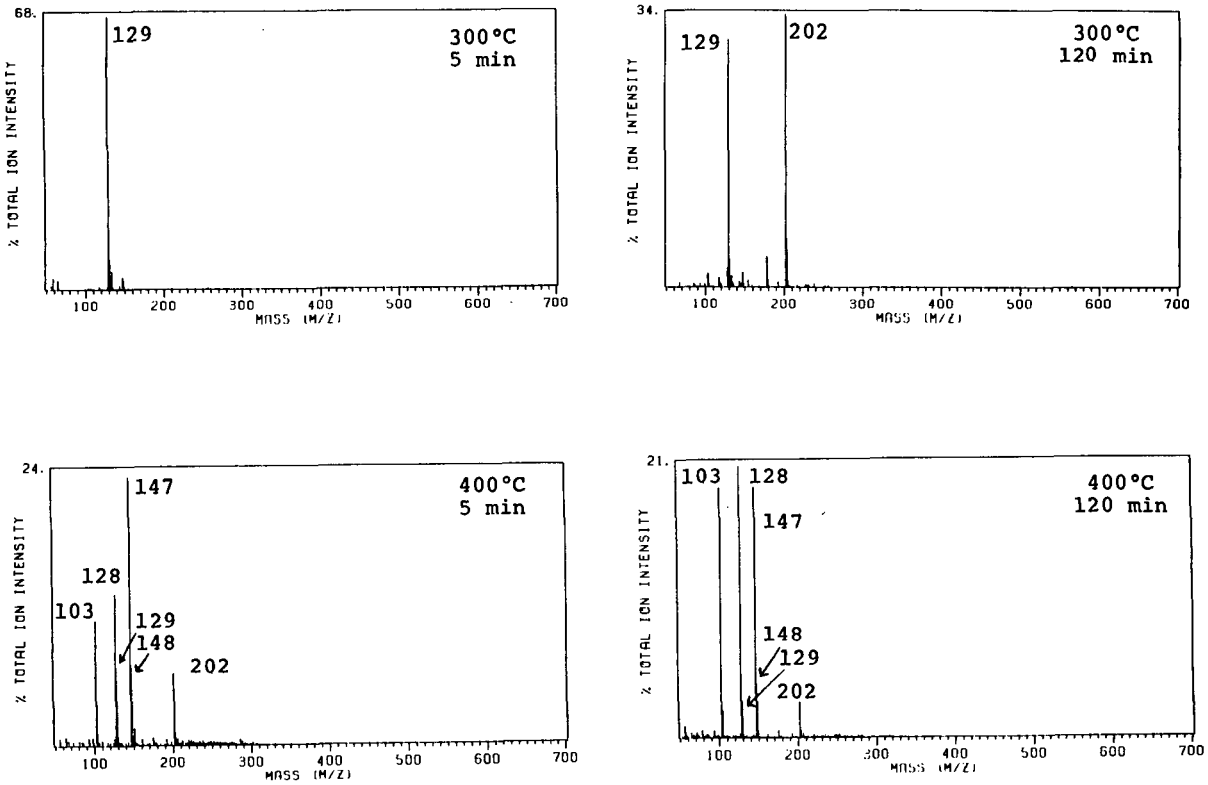
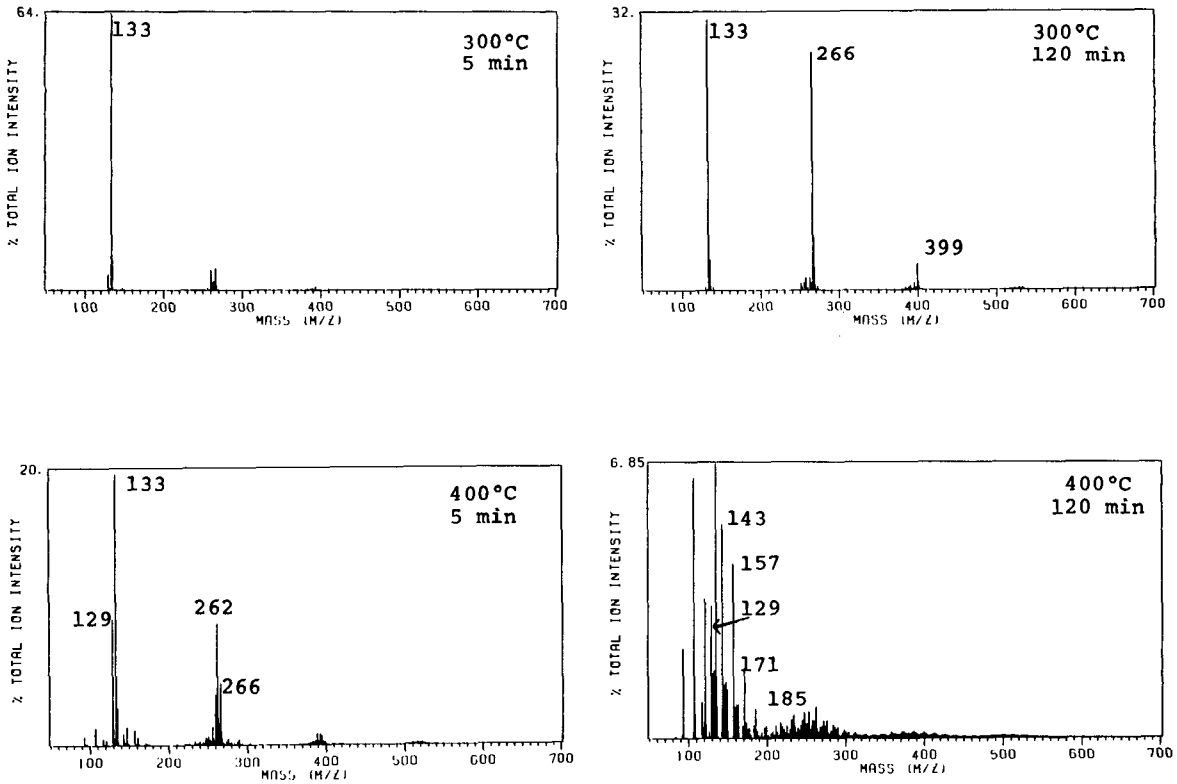



Figure 4. FIMS spectra of liquid products from quinoline HDN reactions.