Shale Oil Value Enhancement Research

Quarterly Report

March 1 - May 31, 1996

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Summary Management Report

The quarter's efforts were concentrated on (a) compound type analysis of shale oil and its extraction products, (b) thermal hydrodealkylation of the >290 °C polar fraction, (c) reaction of pyridinic type compounds to form secondary products, (d) updating SPX economic analysis, and (e) preparation of a business plan for presentation before the Dawnbreaker Commercial Assistance Program.

The subcontract on the thermal hydrodealkylation work at the University of Utah ended at May 31, 1996. We have obtained valuable information from the batch experiments. The progress on the flow reactor proved somewhat limited because of the restriction of the existing reactor configuration. The THDA work is continuing at JWBA with a smaller scale operation.

The liaison with potential industrial partners is continuing. An additional company has reached agreement to proceed with agrochemical testing of shale oil derived products. The other important progress is that we have been invited to participate as a finalist in Commercial Opportunity Forum of the Dawnbreaker Commercialization Assistance Program. We qualified for their program because the initial thrust for value-added products (tar sands bitumen) research originated in the SBIR program. During this quarter, we have received supporting documents from three possible shale oil producers (who are also potential investors) in supporting the shale oil development plan. This support strengthens the business development plan and makes the commercialization more feasible.

Overall, the project is on schedule and on budget.

Technical Progress Report

Objectives for the Quarter were:

- Continue flow THDA of S.O. >290 °C polar fraction and analysis of THDA products,

- Conduct potentiometric titration and IR analysis on S.O. extraction products for basic nitrogen determination and compound type analysis,

- Investigate reaction types (e.g., oxidation, chlorination, and polymerization) of the <290 °C shale oil extract fraction in order to obtain higher value products;

- Continue industrial liaison, market evaluation and prepare commercialization business plan.

Discussion

Task 8. Separation Development

Determination of Basic Nitrogen Types To determine the basic nitrogen types of the shale oil, four shale oil fractions are titrated with 0.1 N perchloric acid in glacial acetic acid under varying solvent conditions at 50 °C. We have found that only at this temperature the precipitation problems are minimized and the results are more reproducible. Acetic acid, acetic anhydride, and a mixture of the two were used as solvents with toluene to improve solubility. The titration was recorded with a Mettler DL40RC automatic titrator using a nonaqueous combination glass electrode.

Since 5-membered ring heterocycles for the most part are too weakly basic to be titrated, quantitation of pyrrole, indole, and carbazole are accessed by IR technique. The N-H stretching were measured at around $3400 - 3500$ cm^{-1} of pyrrole (as standard) and shale oil samples dissolved in CCl_4 solvent. The results are summarized in Table 1.

Table 1. Analysis of Basic Nitrogen Types in Shale Oil Samples

Sample	Shale Oil Sample			
	Total S.O.	<150°C frac.	>150°C frac.	>150 Extract
SPX ID #	28-95-465	29-96-48	28-95-408	28-95-462
wt. frac. of total SO	1	.05	0.95	0.40
weight % N	1.58	.25	1.65	3.33
Total N (m mol/g)	1.13	0.2	1.18	2.38
Probable nitrogen by type (m mol/g)				
Aryl Amines	0.0	0.04	0.0	0.0
Alkyl Amines	0.0	0.0	0.0	0.0
Pyridine type	0.51	0.16	0.57	1.29
Pyrroles*	0.16	0.0	0.18	0.41
Misc.**	0.46	0.0	0.43	0.68

* include pyrroles, indoles, carbazoles.
** miscellaneous (by difference) includes N-substituted pyrrolic compounds, nitriles, amides, the second nitrogen of compounds having two or more nitrogens.

As indicated by Koros and coworkers (1967), aryl amides are determined by the difference of amount of titrant used between using acetic acid solvent and mixed solvent (1:1 acetic acid + acetic anhydride). Alkyl amides are determined by taking the difference between total titrant and amount of titrant used to reach half neutralization point (HNP) from strong to weak peak when using acetic acid solvent, and the amount of aryl amine deducted. The HNP of the aryl and alkyl amides (in acetic anhydride) are in the range of 300-550 mV. Pyridines are determined from the amount titrant employed to reach HNP from strong to weak peak in acetic acid solvent. The HNP of pyridines in acetic anhydride solvent are below 300 mV. Pyrroles plus miscellaneous are considered non-titratable.

As indicated, almost all of the nitrogen in shale oil are within the nitrogen heterocycles, in which pyridine is the most abundant (well above 50 %) nitrogen compound found. Although more concentrated in the higher boiling fraction, pyridines are also found in the below 150 °C boiling

fraction. The amount of pyridines (mostly picolines) which appear in the below 150 °C fraction is about one weight percent. With an average molecular weight of 300 of the extract, the amount of pyridines is estimated to be about 39 weight percent. The balance contains 33% nitrogen compounds (non-pyridinic types, non-titratable, e.g., indoles) and 28% non-nitrogen compounds, probably phenols and polar oxgyen compounds as discussed below.

Acid-base Separation   The purpose of this work is to both help quantify the type of polar compounds present and to obtain a better understanding on their thermodynamic behavior. We have prepared anion and cation exchange resins for separating acid and base fraction of the shale oil samples. The detailed preparation procedures can be found in the previous Monthly Report (SPX2-39-96, April 20, 1996).

Two formic acid extracted polar shale oil samples, 31.3 grams of the >150 °C and 20 grams of 150-290 °C boiling fractions, were each dissolved in 200 cc of cyclohexane and separately charged to the anion exchange resin column. Unadsorbed material was washed from the resin with 200 cc of pentane (with recycle) for approximately 6 hours. The adsorbed material (acids) was recovered by successive elutions with methanol followed by methanol saturated with CO_2. The acid-free sample is then introduced into the cation exchange resin column, procedure similar to that of the anion exchange step. The adsorbed material (bases) was removed from the resin by sucessive elutions with methanol followed by 8% isopropylamine in methanol.

The results of the acid-base separation are quantified and tabulated as follows:

Table 2. Analytical Data on Shale Oil Extracts (in weight percent*)

Sample ID	Boiling Range, (wt.% of total SO)	Acid	Base	Neutral
SPX29-95-462	>150 °C, (~40%)	17.8	50.3	31.9
SPX29-96-111	150-290 °C, (~15%)	15.8	40.5	43.7

*Values are normalized, the total percent recovery of both separations are slightly above 100, due to the presence of solvents.

The acid-base separation further confirmed that the amount of base fraction is about 20% of the total shale oil. Each of the separated fraction was then subjected to GC/MSD analysis and the total ion chromatograms are shown as Figure 1 and 2. It was found that the major components in the acid fractions are phenols. The minor acid types include carboxylic acids, naphthalenols, and

benzothiophenes. The major components in the neutral fractions are paraffins, cycloparaffins, and alkylbenzenes. The minor neutrals types include olefins, naphthalenes, and phenanthrenes, etc., as determined by the Wiley library of MS fragmentation patterns.

The major components in the base fractions are alkylpyridines. The minor base types include quinolines, pyrroles and indoles. The significant skew toward longer retention time of the base fraction suggest that the basic materials are preferentially found in the higher molecular weight species. The alkylpyridines seem to be more concentrated in the higher boiling regime, which is consistent with the results of the n.m.r. analysis.

Within the next period, we will perform the acid-base separation on the raffinate fractions and try to close the material balance. With the paired extract and raffinate information available, we should be able to assess the separation efficiencies of the extraction process.

Task 9. Conversion Development

Thermal Hydrodealkylation (flow mode) We have made five flow THDA runs of > 290 °C polar fraction at the University of Utah. The reaction conditions were reaction temperatures of 505 to 535 °C and 1000 to 1500 psig hydrogen pressure. The calculated gas residence time is between 0.6 to 3 seconds. Although the liquid products are apparently brighter and less viscous, the GC analysis showed no more than 15 % yield of light product from the hydropyrolysis of the heavy fractions. The apparent brighter color and lower viscosity could also result from the cracking of the solvent (methylcyclohexane).

The results obtained from the flow THDA at the University of Utah showed limited yields. The THDA reactor was adapted from a previous coal hydropyrolysis reactor and its operating conditions falls into a "blind" region in which the desired process severity can not be achieved without major revision of the reactor configuration and extensive experimental work. This is due to the fact that the reaction has to be operated at fairly low residence time (<3 seconds) to reduce the potential plugging inside of the horizontal reactor tube. In the mean time, at maximum reaction temperature of 535 °C (with the current configuration and limited heat source) and short residence time, the process conditions are not severe enough to achieve the desired yield. Our experience showed that the better reaction temperature and residence time combination would be 535 °C and 20 seconds or >600 °C for under 3 seconds. Neither of these conditions can be achieved with the current configuration.

After careful evaluation, we would like to pursue the THDA work in two directions:
1) continue the batch THDA in a miniature bomb reactor, and
2) assemble a simple down flow reactor system within the JWBA laboratory. With the reactor system set up on site, we believe that the THDA work can be carried out more effectively.

With most of the component available, we expect to assemble the working unit within a

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month and reinstate flow experiment before the end of July. The decision as to whether to proceed in this direction will depend on the likelihood of receiving funds to complete the project. If Phase-III funds are not forthcoming, it will be more prudent to use the available funds to focus on certain of the Phase-III market assurance efforts. Without market assurance, we have little chance of attracting private capital.

Thermal Hydrodealkylation (batch mode) In parallel to the effort of flow THDA at the University of Utah, several bomb hydrodealkylation experiments were performed using a 50 cc stainless steel Hoke bottle. The bomb is equipped with a thermocouple and a precision pressure gauge. A small amount of oil sample (neat) was heated up to the desired temperature in a relatively short period. The general procedures of the experiments are reported in the previous Monthly Report (SPX2-40-96, May 22, 1996). Table 3 summarizes the results of these experiments.

TABLE 3. Comparison of yields of batch THDA runs.

Exp. #	Temp. °C	Additive	Wt. % Coke	Wt. % Gas + Liquid
1	540	---	21	79
2	540	$AlCl_3$	52	48
3	510	---	15	85
4	510	$AlCl_3$	16	84

Figure 3 compares the first 30 min. (<300 °C) of Total Ion Chromatogram (TIC) of the liquid products obtained from the non-catalytic experiment #1 (540 °C) and #3 (510 °C) . It is found that the lower temperature run preserves more paraffinic and olefinic products (resulted from dealkylation) whereas the higher temperature run shows very little aliphatic hydrocarbons. The lower temperature run also produced relatively much less pyridinic products. These results confirm earlier work that some critical temperature above 525 °C is needed for significant conversion at short residence time.

Figure 4 shows the first 30 min. of the Total Ion Chromatogram (TIC) for liquid products obtained from reaction temperature at 510 °C. The top TIC is obtained from a thermal run (Exp. # 1) and the bottom TIC is from a run (Exp. # 2) with addition of $AlCl_3$. The addition of $AlCl_3$ appears to enhance the production of the picolines and lutidines and reduce the relative amounts of the C_5 and C_6 Pyridines. The $AlCl_3$ has reduced the relative amounts of heavy ends in favor of the lower boiling analogs. The overall conclusion is that the $AlCl_3$ increases the rate of dealkylation reactions. However, the high coke formation at 540 °C and in the presence of $AlCl_3$ suggests that use of $AlCl_3$ would not be commercially viable.

Aluminum chloride is a mild Lewis acid and has traditionally been used as a Friedel-Crafts alkylation catalyst. Ipatieff and coworks (1937) has studied dealkylation of alkylbenzenes with $AlCl_3$ catalyst. It is obvious that the performance of the acid catalyst would be less effective because of the basicity of the pyridinic compounds. The addition of $AlCl_3$ in this study indicated that the catalytic effect is rather complicated. The benefit of larger yield of lower alkylpyridines is suppressed by the higher yield of coke. The results of this study confirm our initial concern that performing dealkylation using acid catalyst at higher temperature is rather impractical.

TASK 10. Product and Process Integration

Chlorination of the Pyridinic Compounds: The chlorinated pyridines are intermediates of many agrochemicals. For example, 2,3,4,5-tetrachloropyridine can be converted to the insecticide chlorpyrifos, and trichloropyridinol was converted to the herbicide trichlopyr. Direct chlorination can be achieved by the contact of chlorine and pyridine in the vapor phase. The alkyl-substituents of the alkylpyridines block the (chlorinating) sites and make chlorination more difficult than that of the unsubstituted pyridine. We have successfully synthesized chlorinated pyridines and a mixture of lower alkyl pyridines (obtained from a commercial source) in the JWBA laboratory. An example chromatogram of a mixture of chlorinated pyridines is given as Figure 5. Work toward shale oil derived alkylpyridines is under way. Initial results showed that the residual olefins remain in the SO-derived-alkylpyridines are easier to be chlorinated. Under the same operating conditions, chlorination of the SO-derived-alkylpyridines tends to form much more polymerization products. The degree of chlorination and polymerization is strongly associated with the reaction temperature. To minimize polymerization reaction, the chlorination of the SO-derived-alkylpyridines needs to be carried out at a carefully regulated environment. Derivatized samples will be submitted to our agrochemical testing partners to measure biological activities for pesticides, herbicides, and fungicides.

In addition to chlorination reaction, we are also investigating quarterization and oxidation reactions of the alkylpyridines. Other possible applications of SO-derived-alkylpyridines are:
- a. corrosion inhibitor
- b. additive for paving materials
- c. additive for metallurgical oils

We are gathering additional published data and consulting with experts on these possible applications.

The liaison with potential industrial partners is continuing. An additional company has reached agreement in principal to proceed with agrochemical testing of shale oil derived products. This brings to three the number of companies actively pursing identification of new product opportunities.

Task 11. Simulation and Economics

We have submitted a draft of business plan entitled "Pyridines from Shale Oil" for the presentation before the Dawnbreaker Commercialization Assistance Program. After the reviewing, we were notified that we achieved a high score and are being invited to participate the final Commercial Opportunity Forum next October. During the next period, a list of suggested attendee will be prepared and the final Business Plan polished.

During this period, we have received supporting documents from three shale oil producers (who are also potential investors) in supporting the shale oil development plan. This support strengthens the business development plan and makes the commercialization more feasible. The marketing effort will proceed until a major investor commits to the development plan (hopefully before the end of this project).

We have argued that full funding of Phase-III (~$650K) would greatly enhance our market assurances of the product slate and raise the probability that we would partner with industry for full-scale development. We are seeking the funding to complete the Phase-III work through the industry. However, without Phase-III results, the SPX development plan will be less attractive because there will be greater risks in assuring buyers of the products marketability at the price projected. However,

Objectives for the Next Period

- Assemble reactor modules for conduct flow THDA and reaction of alkylpyridines at elevated conditions,

- Perform acid-base separation on the raffinate fractions and assess the separation efficiencies of the extraction process,

- Perform reaction types (e.g., oxidation, chlorination, and polymerization) of the <290 °C shale oil extract fraction in order to obtain higher values products;

- Refine commercialization business plan, proceed with industrial liaison and update market evaluation.

Figure 1

Total Ion Chromatograms for the Acid, Base, and Neutral
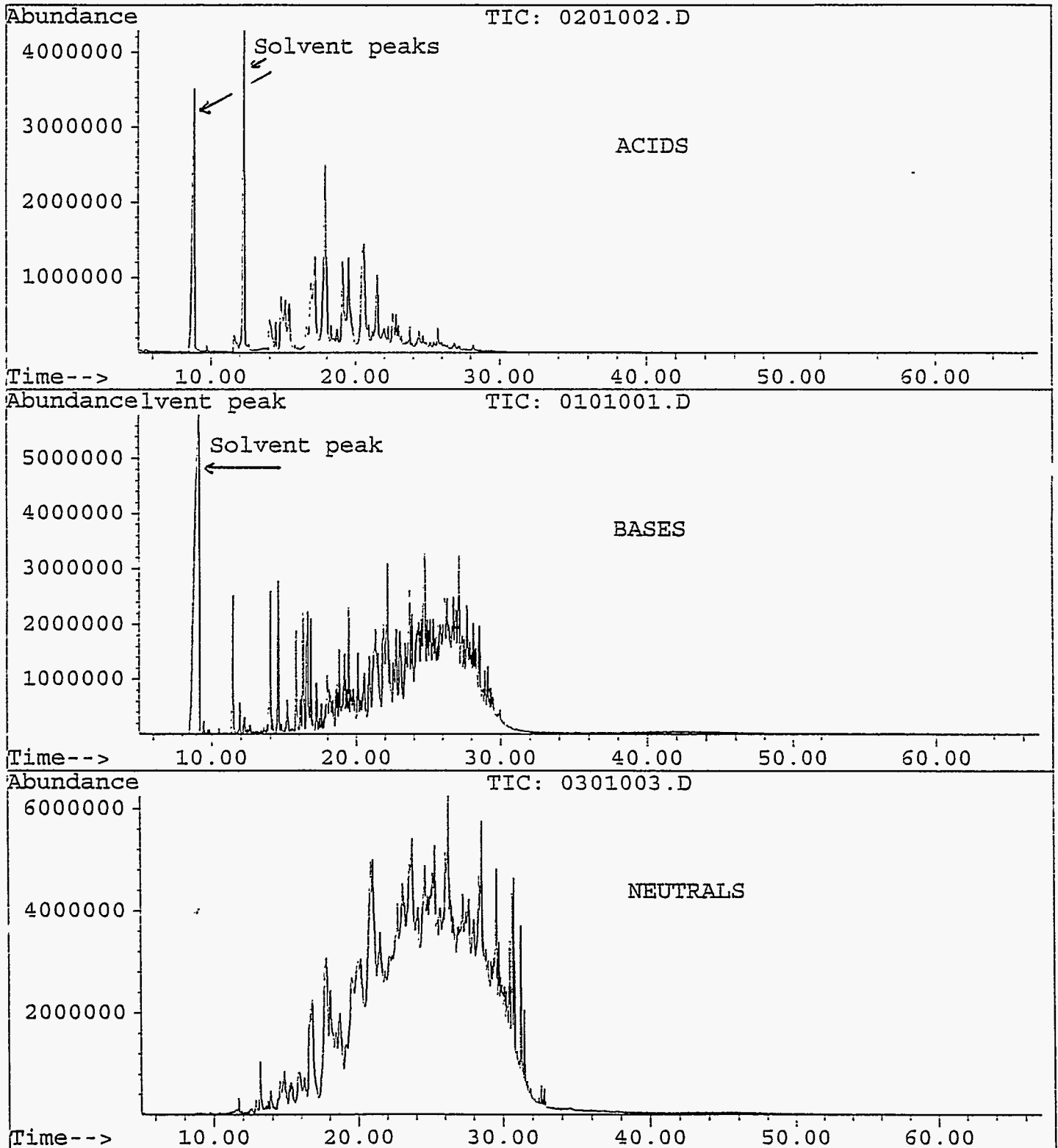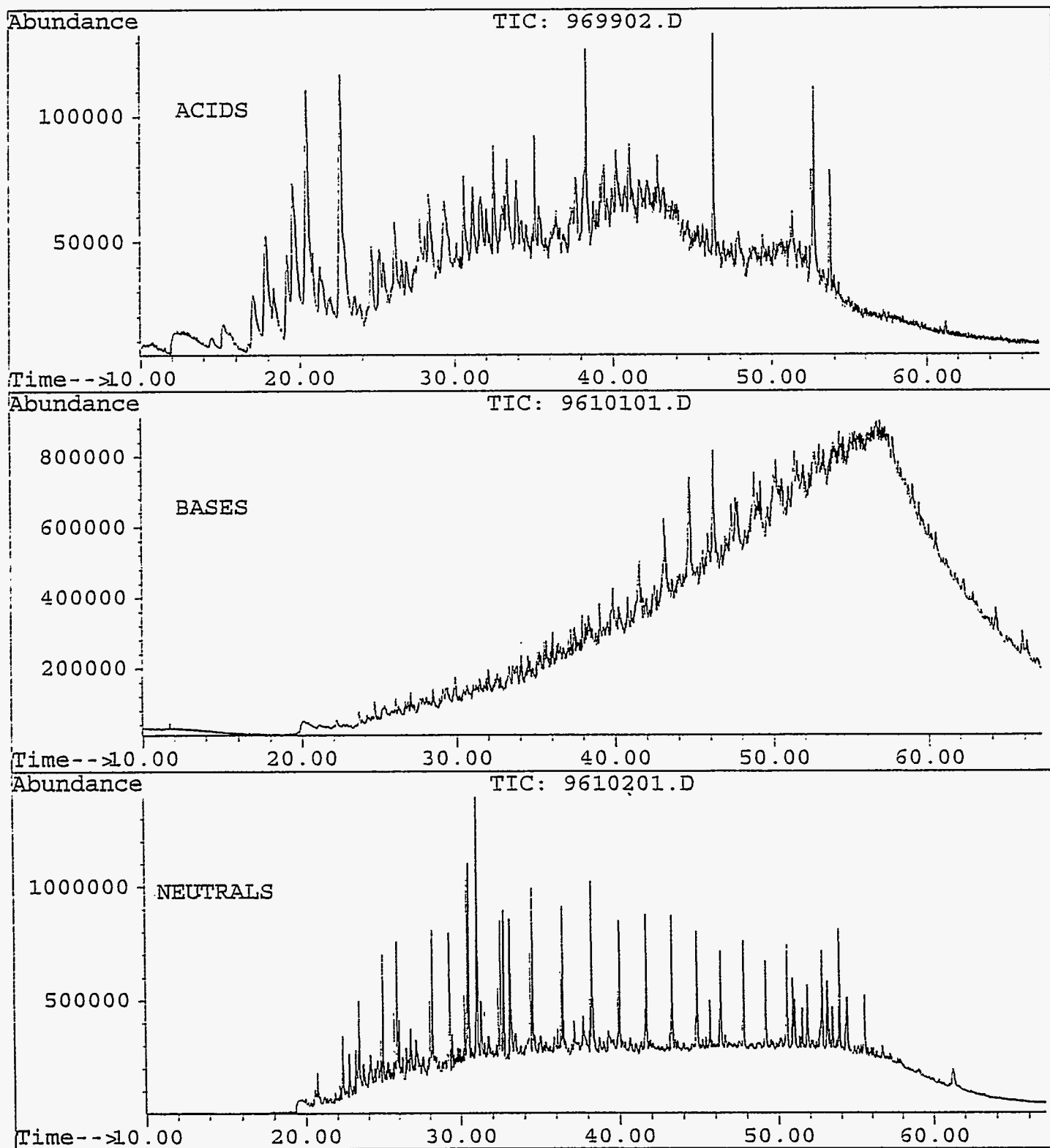Compounds From the 150-290 °C Fraction

Figure 2

Total Ion Chromatograms for the Acid, Base, and Neutral
Compounds From the >150 °C Fraction

Figure 3. Comparison of TICs of liquid products obtained from batch THDA experiments; (a) 540 °C run and (b) 510 °C run.
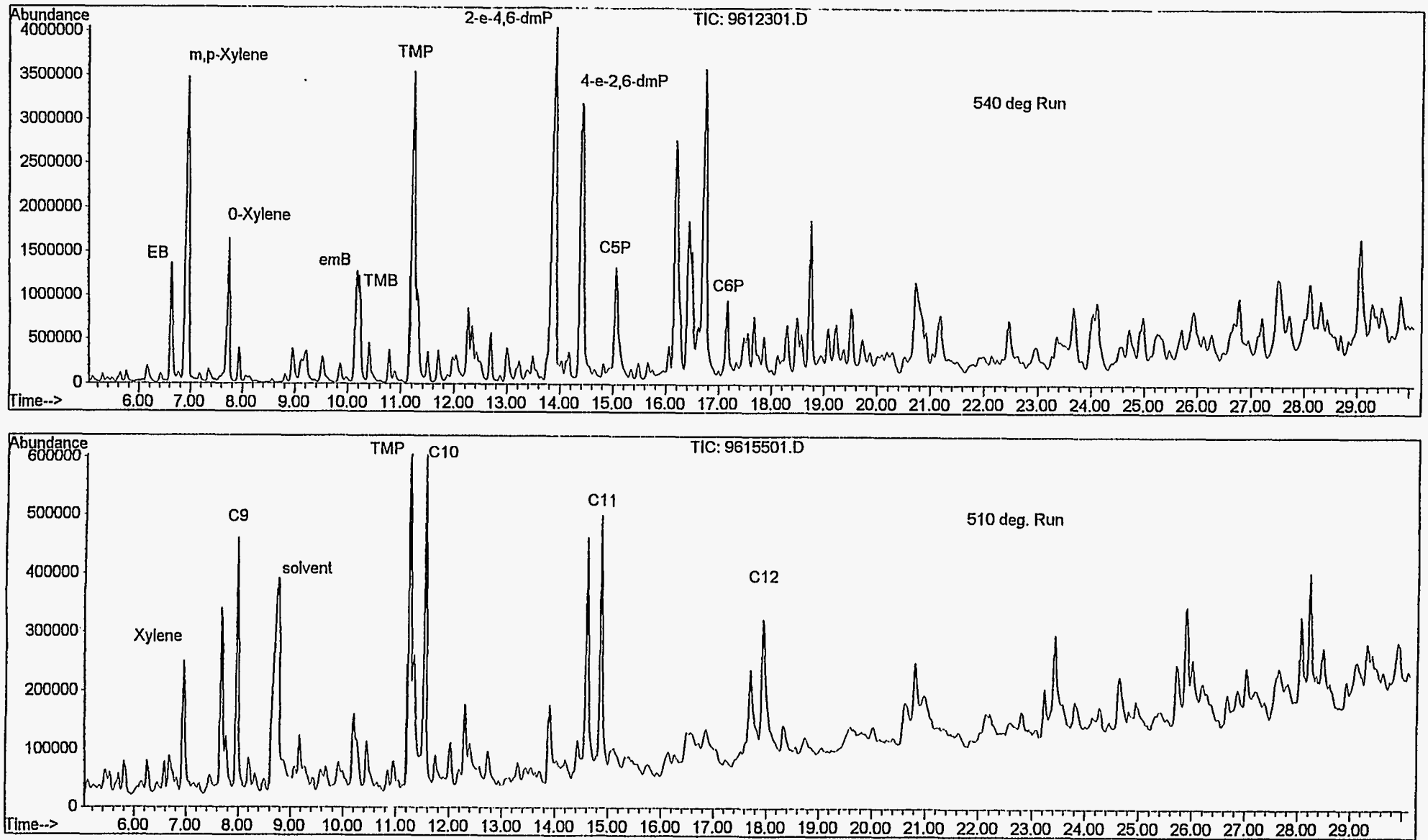
Figure 4. Comparison of TICs of liquid products obtained from batch THDA experiments at 510 °C; (a) no additive and (b) with addition of AlCl₃.
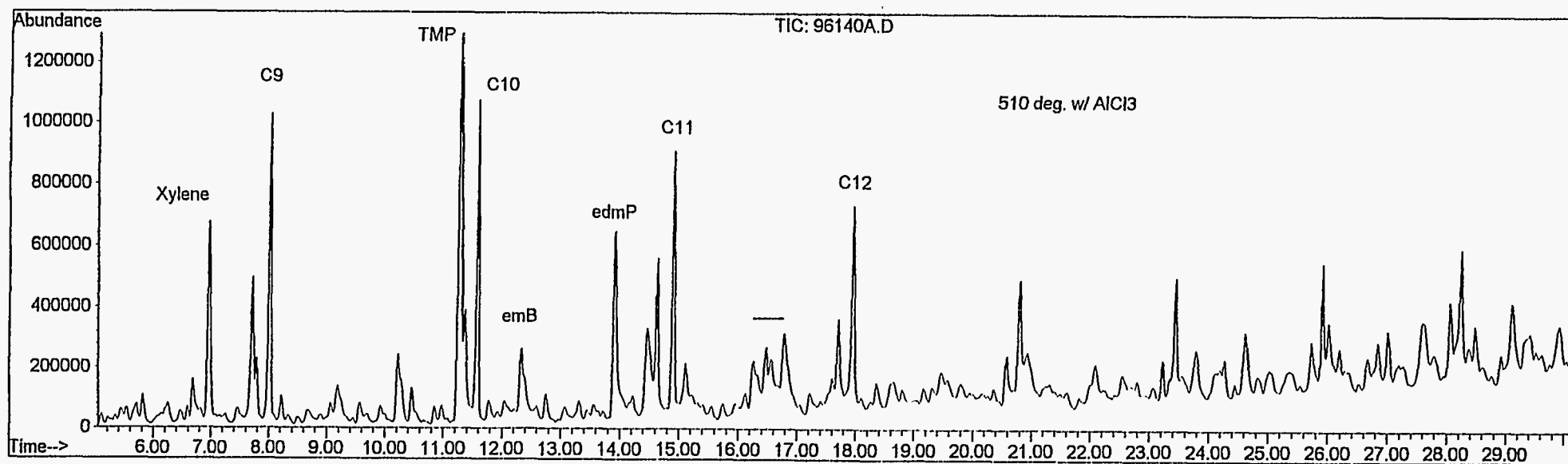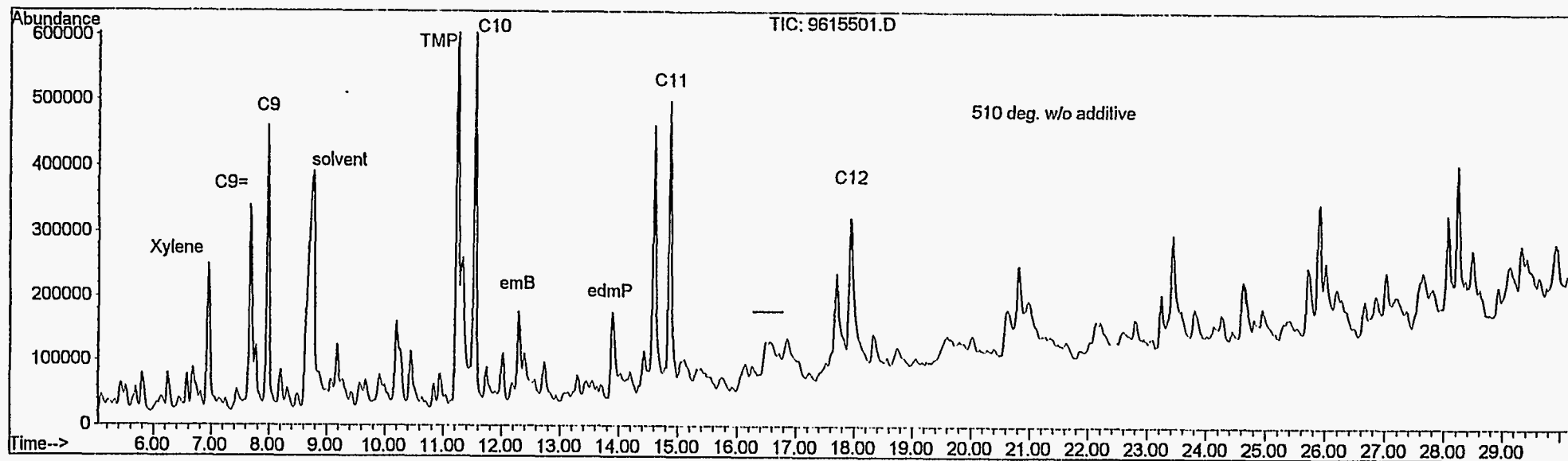
Figure 5. Chromatogram of chlorinated pyridines obtained from direct chlorination of pyridine.