

Shale Oil Value Enhancement Research

Quarterly Report
December 1, 1994 - February 28, 1995

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Summary Management Report

The quarter's efforts were aimed towards completing phase-I. We expect to complete phase-I in the next quarter. The final in phase-I will produce the new economic estimates to use as guidelines for phase-II activities.

Progress on phase-II has been initiated with the focus being on completing fabricated equipment needs. One result of phase-I is the simplicity in process strategy. The ability to pool the +200 °C polars prior to THD is one such simplifying step. Ultimately, the elegance of a shale oil value enhancement scheme will come from maximizing the value while minimizing the number of process steps. A scheme with these characteristics is what is emerging from phase-I.

An effort is being made to attract private investment funds in JWBA, part of which will be earmarked specifically for a special effort in completing an agreement with a commercial partner. With an agreement with a commercial partner in place, it is believed that a request for federal cost sharing for the next phase of development in FY '97 and beyond will be warranted.

Technical Progress Report

Objectives for the Quarter were:

- Perform six-stage extraction of total shale oil using the dual solvent system
- Complete modifications to the extraction unit to extract +400 °C fraction
- Conduct hydrodealkylation experiments on the shale oil fractions
- Complete cost and economic analysis for both schemes
- Continue marketing efforts aimed at identifying additional majors as candidate partners for commercialization

Discussion

Task 1.

The NEPA task has been completed. Approval for CX-B has been granted for Phase-I on June 20, 1994 and for phase-II on December 19, 1994.

Task 2.

The separations characterization task is completed.

Task 3.

The analytical methodologies development task is completed as needed for phase-I. In phase-II, these analytical methods will be tested and used to evaluate the efficiency of separation processes. As reported in our previous quarterly report, the property prediction methodology has been extended to include other properties. The ZNUMP program has been tested on the conversion fractions. A detailed description of the program and its output are presented in the task-6.

Figures 3.1 to 3.4 show the correlation between actual and calculated values of vapor pressure, density, viscosity and gravimetric heat of combustion. The fit is very good for the selected compounds. Other properties correlated include: solubility, refractive index and melting point. Except for melting point, all other properties correlated well with enthalpy and entropy differences between the compound and its corresponding paraffin. The significance of this effort is that this methodology enables us to calculate properties of interest to track partition behavior from GC-MS runs without having to know the structure.

Vapor pressure, density and viscosity properties are important to the design of distillation system and extraction systems including solvent recovery and quality of solvent (build-up). By developing these correlations we avoid the need for actual measurements on experimental fractions.

In the phase-II, these correlations for prediction of properties and partition coefficient methodologies will be applied to the separation processing design for shale oil fractions. Some refinements may be necessary when dealing with complex mixtures. The development of analytical methodologies has reached the stage where further work will aim at improvements rather than basic development. These methods and tools are expected to save time in the routine analysis and improve our understanding of separation process characteristics of shale oil.

Task 4.

Market research task has been completed and results as reported in our previous quarterly reports illustrate the market potential of products from shale oil as identified in the phase-I. No additional market qualification work is contemplated at this stage until we get some qualified samples. Any follow-up results from our previous contacts will be reported in relevant tasks.

It is important, however, to pursue the leads to attract a partner for commercial venture early in the phase-II. Efforts will continue to explore all avenues to contact new leads and keep previous contacts informed about the progress of the work. It is conceivable that many of these potential commercialization partners are eager to see final qualified samples and results before making any commitments. We hope to achieve this goal as soon as possible.

Activity testing work by Company A resulted in no exciting information due to the fact that fractions were broad cuts. The biological and/or agricultural activity, which is due in part by heteroatom containing compounds, is masked by other competing hydrocarbons. In our discussions we have been told that specific activity can often found in only a few compounds, but these compounds may be particularly powerful. Our license agreement also includes compounds which are synthesized using shale oil as a starting material. It is also important to note that long side chains of these molecules are not desirable for exhibiting any activity. In conclusion, the next batch of samples for activity testing would include but will not be limited to dealkylated extracts for various narrow-boiling shale oil fractions. It is anticipated that this approach will enhance the activity and yield more positive results.

In the future, marketing efforts will be continued with a specific goal of achieving an agreement with a potential commercial partner to participate in the development and commercialization.

Task 5.

The separations explorations task has been completed. Any related results will be reported in separations development task of phase-II.

Task 6.

During this quarter, a bomb reactor has been designed, fabricated and operated to study dealkylation of shale oil fractions. Thermal cracking reactions were conducted to dealkylate the shale oil fraction and thus reduce molecular weight. The purpose of this work is to better assess what nitrogen ring structures survive a severe dealkylation environment.

A muffle furnace was used as the heat source. Product is recovered by washing the reactor with a light hydrocarbon solvent. The operating conditions were chosen to avoid coking reactions. The effect of operating conditions such as reaction time, temperature, pressure and reacting environment (H_2 or inert gas) on the extent of dealkylation is being studied.

Figures 6.1 and 6.2 show total ion chromatograms of both feed and product from the thermal cracking experiments. In a batch operation, a wide distribution of boiling points is achieved for the products. It is important to note that significant portion of the product boils below the initial boiling point of the feed. It is also important to note that based on the complete loss of the envelope peaking at about 53 minutes, that essentially 100% reaction has been achieved. In task-9 (phase-II), the reactor configuration will be modified to include recycle the heavy ends to bring the most product into the 1 and 2 ring boiling range.

It is a difficult task to analyze and interpret the complicated fractions of shale oil using conventional analytical methods. To measure the extent of dealkylation, the previously developed Z-BASIC methodology was adapted to monitor the behavior of compound types. Several recent improvements were made to the program including: (a) resolving the isotope peak from the parent peak, (b) adding a quality-of-match test to each ion and (c) refining the probability decisions.

Figure 6.3 shows the ZNUMP program flowsheet, which is the product of Z-BASIC methodology to track compound types. The input to the program is acquired from the integration of GC-MS data. Other inputs include elemental analysis of the sample and boiling point - retention time data to account for changes in the temperature programming. The calculation sequence consists of:

- Isotope Checking
- Calculation of elemental probabilities
- Calculation of possibilities of elemental combinations
- Assignment of molecular formula based on the BP-MW and BP-RT databases
- Checking the quality of match and high probability
- Output sorting routines for compound type distribution and retention time distribution

The testing of the program has been done by comparing its output with Wiley Library using gasoline and the light fractions of shale oil. We use motor gasoline as a test sample because it contains a mixture of paraffins, isoparaffins, olefins and aromatics and possesses a known molecular structure. The output of the program has matched well (better than 90%) and in some cases better.

Table 6.1 shows nitrogen compound types in the +400 °C fraction of shale oil according to ZNUMP program. Based on the GC and elemental analysis data, molecular weights of feed (refer: 3rd quarterly report) and product are 391 and 270 respectively. The average molecular weight of product is reduced by 30% which is the result of paraffin cracking and dealkylation of rings. By analogy, the average molecular weight of nitrogen compounds will also reduce by the same amount.

The total amount of nitrogen containing molecules is calculated to be 29% which is less than 55% reported (as calculated in the 3rd quarterly report). An explanation was found in the decision-making routine of the Z-NUMP program which looks at the highest mass first. If two components co-elute the program assigns the probable compounds to highest mass (the most paraffins or non-polar of the two species) and occasionally ignores lower mass, more polar (and often nitrogen-containing) compounds. Allowing for the fact that the total concentration is nearly double the total shown in Table 6.1, the relative amounts show higher concentrations of quinolines than has been heretofore known. Quinoline and isoquinolines are 4.5 \$/lb commodities, even more valuable than the 3.0 \$/lb for pyridines.

Table 6.1: Distribution of Nitrogen types in +400 °C fraction of Shale Oil (Output of ZNUMP Program)

Compound Type	WT. % in the Feed
Indoles	11
Tetrohydroquinolines	7
Quinolines	5
Pyridines	4
Tetrahydroindoles	2
Total	29

Future work will focus on fine tuning the Z-NUMP program and conduct hydrodealkylation experiments on the shale oil fractions. Any remaining portion of the work will be continued in task 9.

Task 7.

Process modelling efforts are continuing as anticipated. Figure 7.1 shows our economic analysis model for process evaluation. This model is built using spreadsheet modeling tools. The development of process flowsheet is the first step to evaluate the process viability. The data from flowsheet which includes stream information, unit operations and operating conditions are used by both material balance and cost analysis blocks.

Figure 7.1 illustrates the overall connectivity of information flow to conduct profitability studies. Experimental design forms the basis for flowsheet development. The cost analysis block draws information for unit operations from process costs data base which consists of capital cost, utilities, and licensor information for each unit operation. From both material balance and cost analysis, it is now possible to estimate the profitability of the process sequence.

Market analysis data for various products from shale oil imposes limits on the maximum yield of that particular product or compound based on the achievable market share without disrupting the market. If the product yield exceeds the achievable market share, process conditions will have to be modified to change product mix. The information for desired change in operating conditions is expected to be received from the process modeling block.

Profitability measures include internal rate of return, net present value and pay-back period. These calculations are based on discounted cash flow analysis. The sensitivity analysis of various economic factors including capital cost, operating cost, product price and capacity accounts for uncertainties in the cost data.

The economic analysis model has been tested and results will be reported when real data is available. This model will be very useful to evaluate various processing schemes related to various products. The process modelling task has started which includes development of kinetic models for various unit operations. The liquid-liquid extraction process has been evaluated using coefficient of separation and similar approaches will be used to model other unit operations.

Task 8.

During this quarter, the progress in the separations development task was restricted to evaluating the phase-I separations data to design a separations process sequence for phase-II. The planning stage for phase-II effort included the evaluation of the status of various process units required for conducting separations process development work. Table 1 illustrates the status of process units including distillation, extraction, adsorption and precipitation.

Table-1

Process	Scale of Operation	Requirement	Status
Distillation	Pilot	Not needed	Modifications to the existing pilot unit.
Liquid-Liquid Extraction	Pilot	Needed	Increase the existing unit capacity.
Adsorption	Pilot	Needed	Need to be designed & constructed.
Precipitation/ Crystallization	Verification	Not needed	Little commercial risk. But products need to be quantified on a bench scale.

Various modifications to the liquid-liquid extraction unit have been completed. The conversion processing work has been delayed slightly while we complete facilities according to the safety code.

Objectives for the Next Quarter

- Conduct THD experiments to complete the conversions task;
- Complete process modeling task and conduct preliminary economics;
- Conduct process design for phase-II separations development;
- Explore product and process integration strategies;

Figure 3.1: Calculated Vs Actual Log(Vapor Pressure) Differential between a compound and its corresponding paraffin

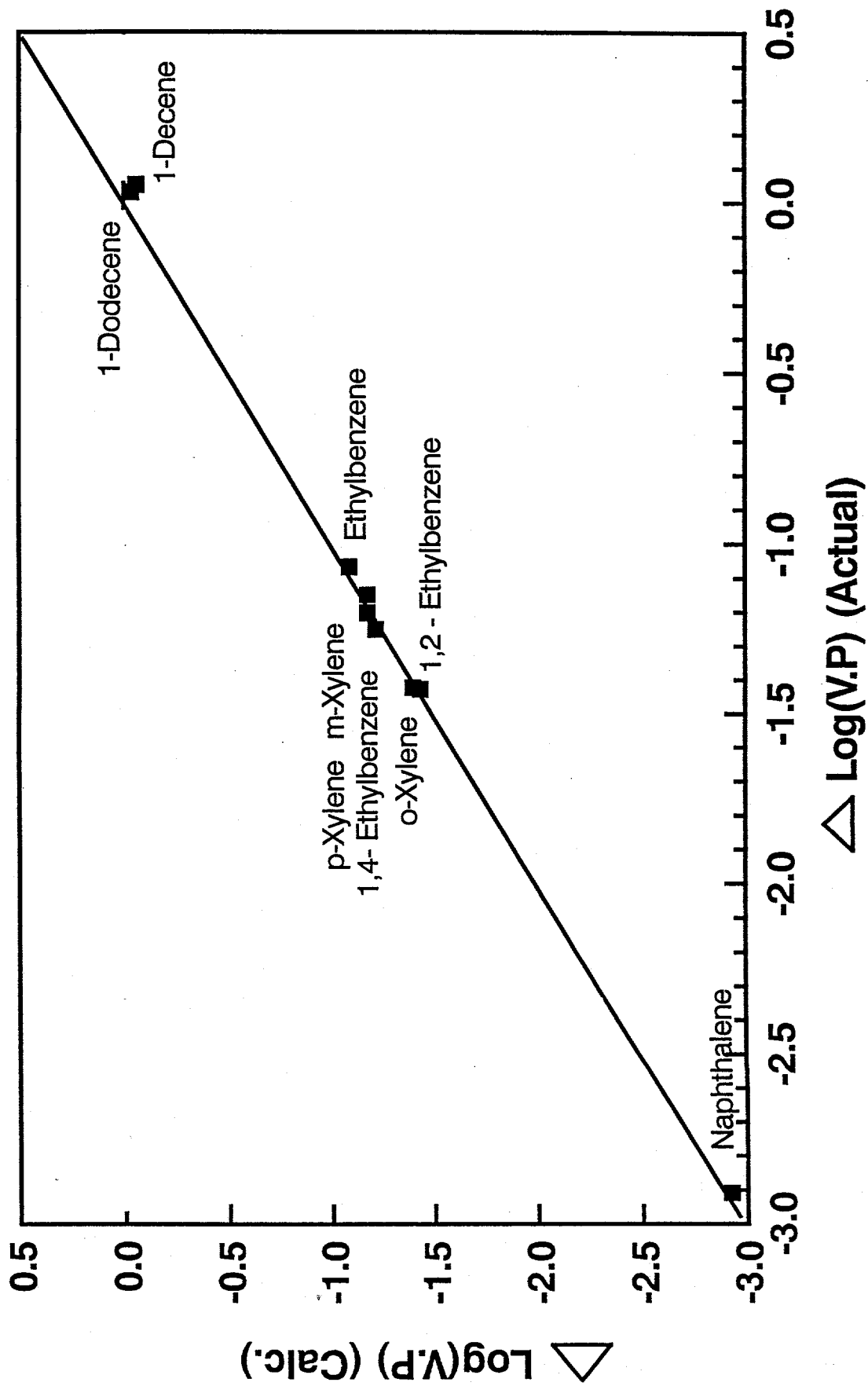


Figure 3.2: **Calculated Vs Actual Density Differential between a compound and its corresponding paraffin**

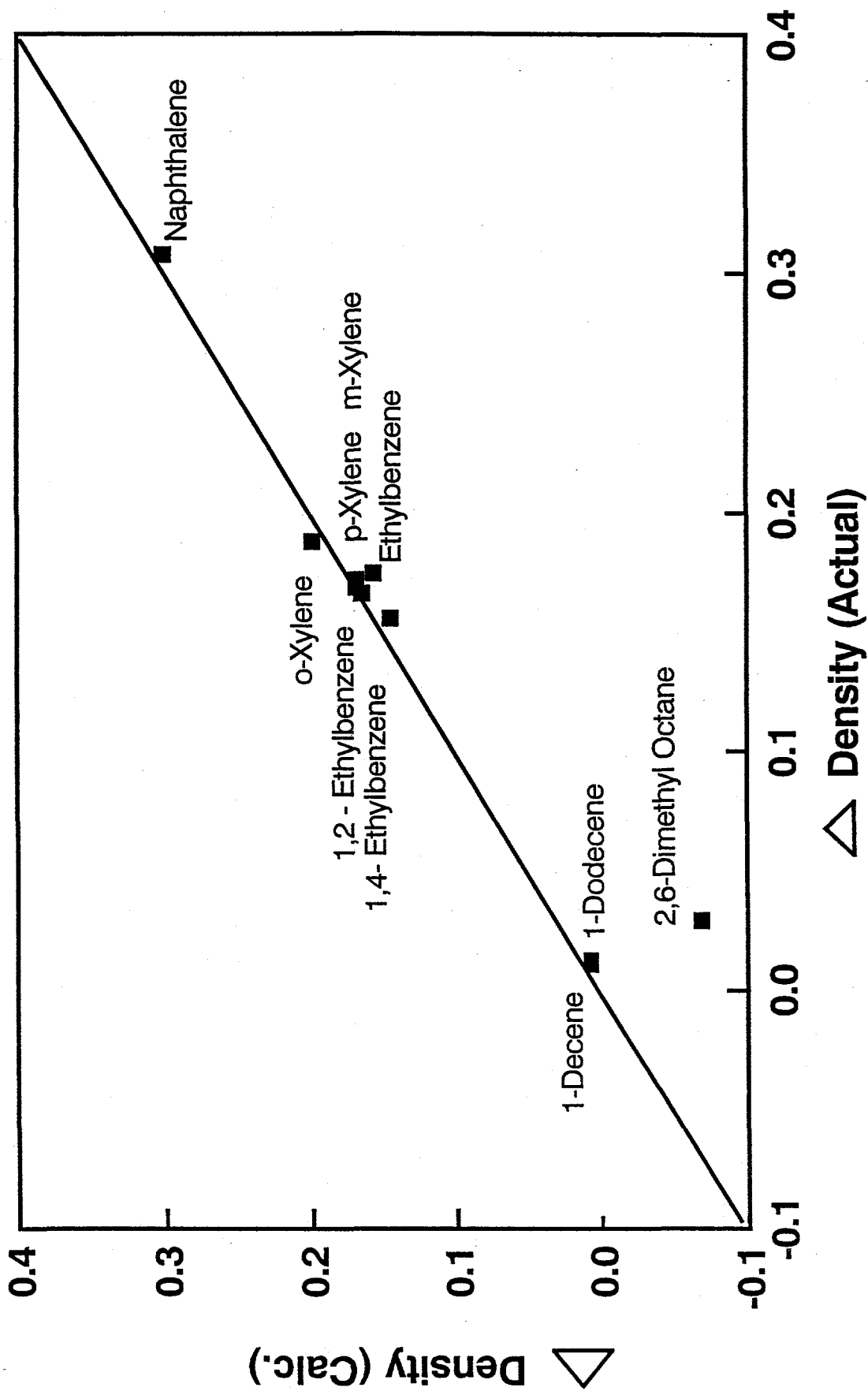


Figure 3.3: Calculated Vs Actual Log(Viscosity) Differential between a compound and its corresponding paraffin

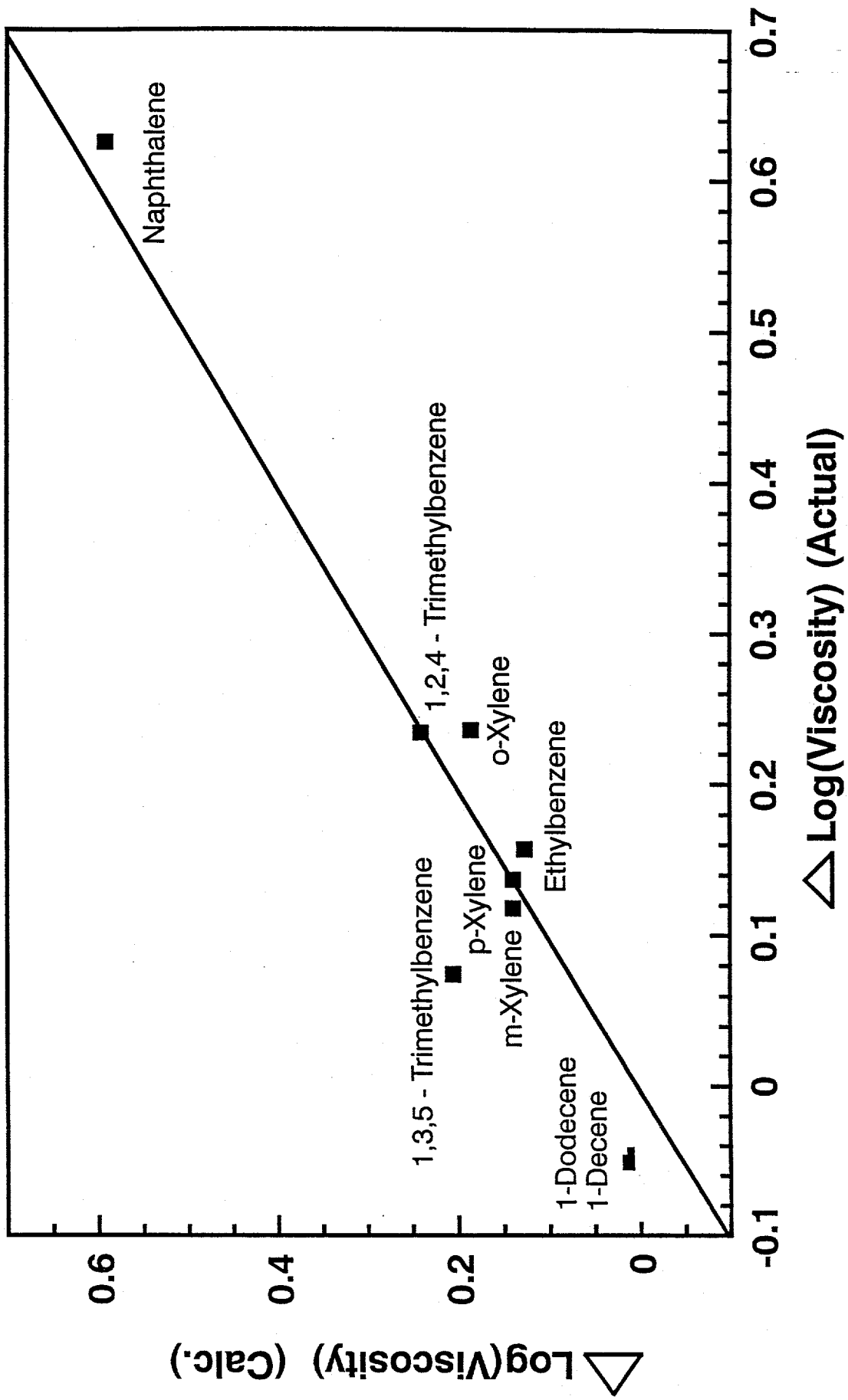
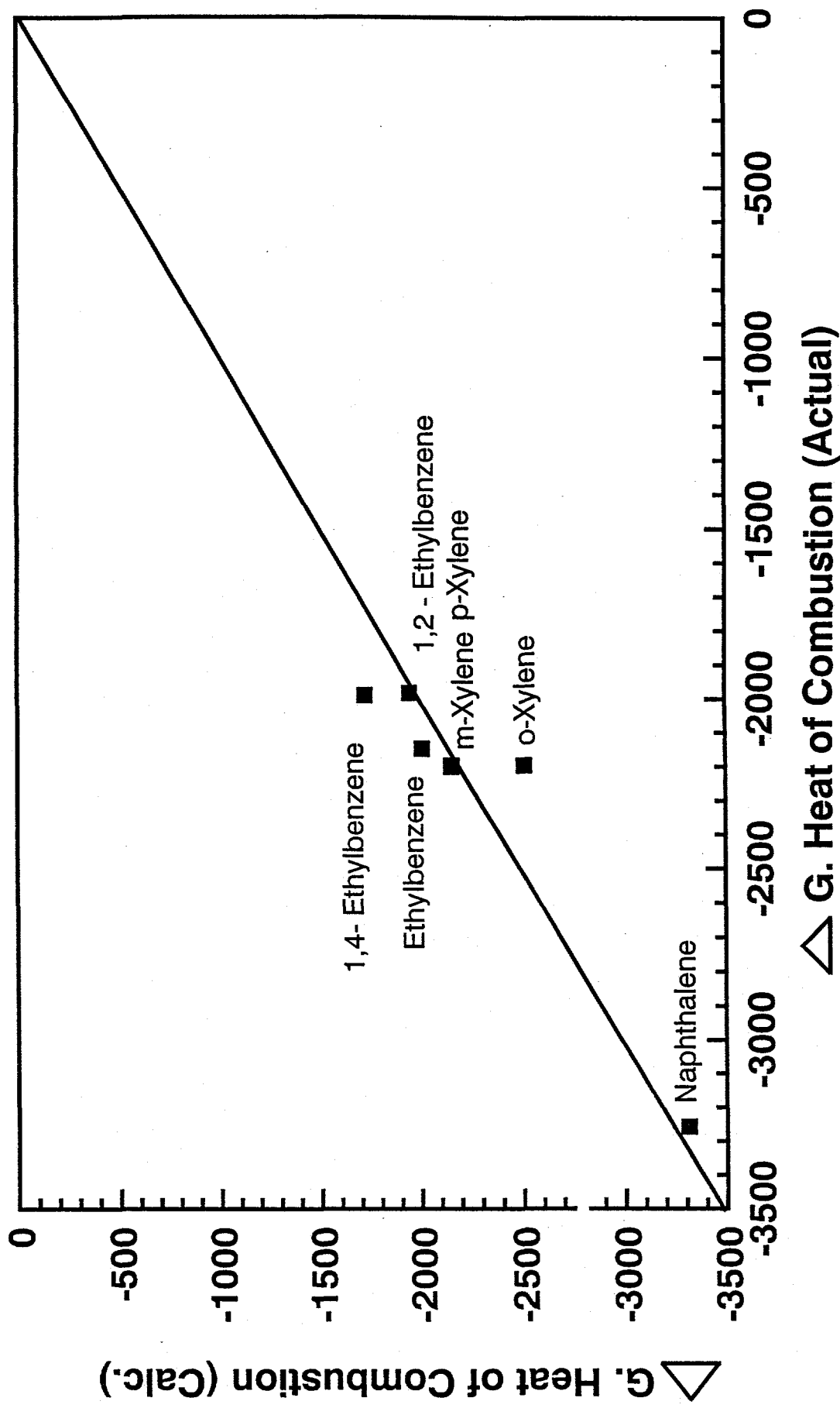


Figure 3.4: **Calculated Vs Actual Heat of Combustion Differential between a compound and its corresponding paraffin**



File : E:\HPCHEM\1\DATA\299367.D
Operator : Don
Acquired : 9 Feb 95 12:55 pm using AcqMethod S09367C
Instrument : 5972 - In
Sample Name: SPX12-93-67 2533mg/l in hexane
Misc Info :
Vial Number: 1

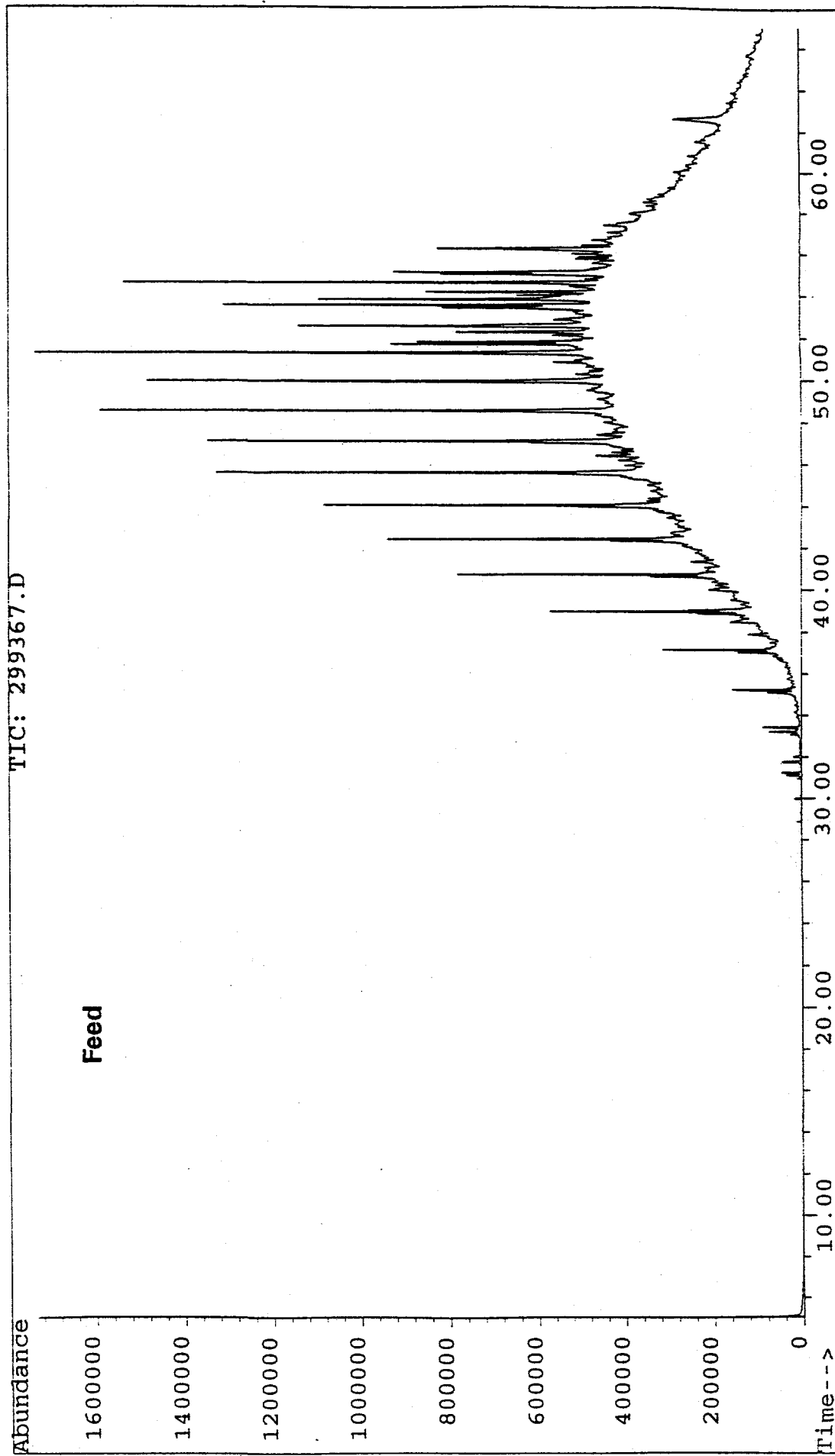


Figure 6.1

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File : C:\HPCHEM\1\S09367\299549.D
Operator : Don
Acquired : 9 Feb 95 3:14 pm using AcqMethod S09367C
Sample Name: SPX16-95-49 in hexane (20g) + Acetone (30g)
Misc Info :

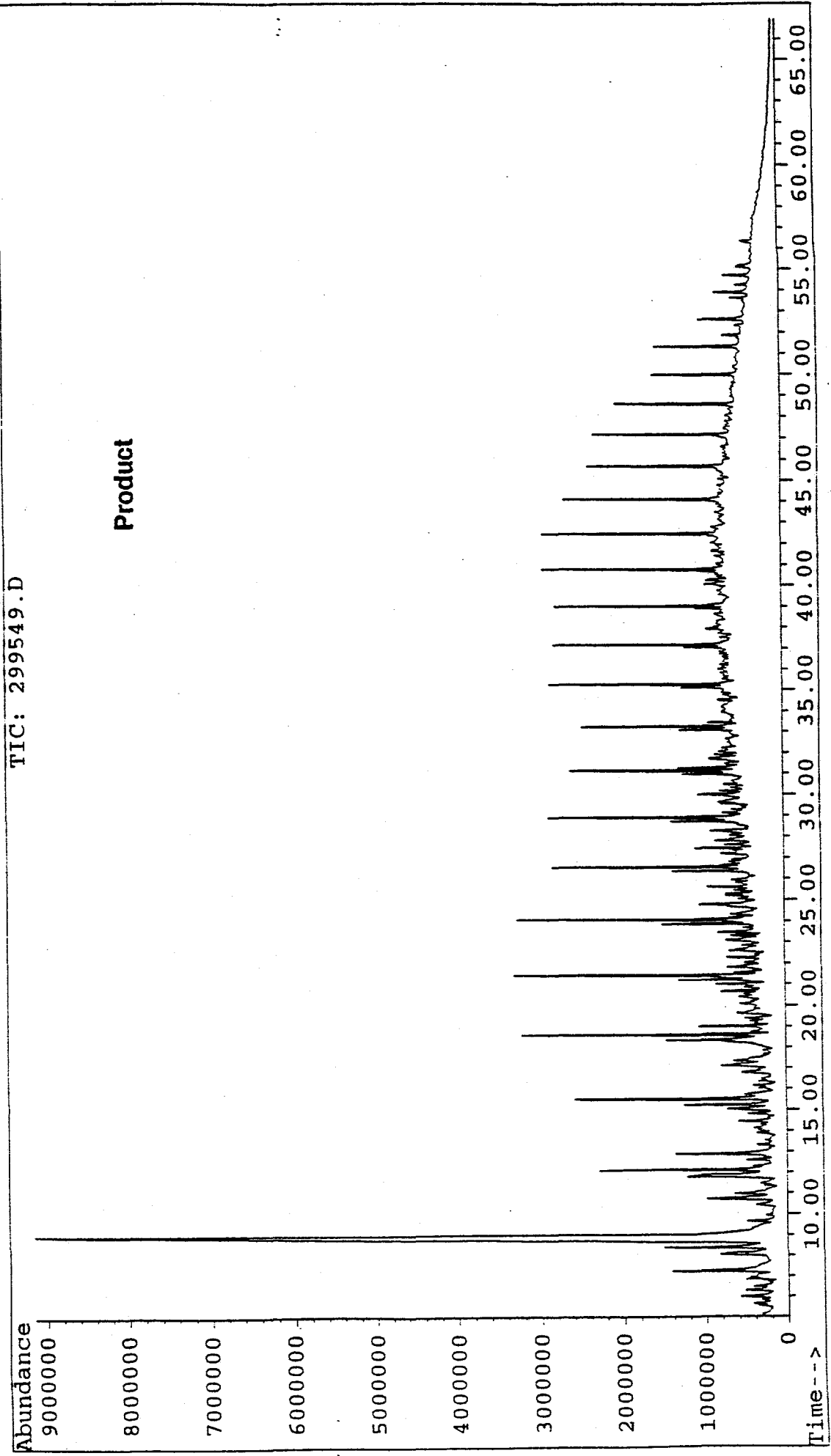


Figure 6.2

Figure 7.1: Economic Analysis Model for Process Evaluation

