

Shale Oil Value Enhancement Research

**Quarterly Report
June 1 - August 31, 1993**

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Summary Management Report

All tasks are on schedule, or ahead of schedule. Particular progress has been made in identifying industrial entities, commodities and specialty products of target interest for shale oil-derived products. There is clearly a major emphasis worldwide on new chemicals and shale oil-derived structures are similar to many of these chemicals of interest.

Details of the mathematical modeling, programming and algorithm development have progressed with excellent results. Considerable effort will be required to interface these with the output of the gc/ms but we are receiving excellent support from Hewlett Packard in this regard.

The ability to concentrate particularly valuable compounds with reasonable projected cost processes continues to show promise. In one system, a single-stage extraction recovered 87% of the total nitrogen in an extract representing only 33% of the fraction. Special attention is being paid to both nitrogen types and oxygen types. The raffinates from the polar solvent extractions will be evaluated for their oil and wax contents.

All of the start-up infrastructure is now in place. Subcontracts have been initiated and equipment and supplies have been procured. We are now planning a major push to reach some general findings by early in 1994. From these findings, we will be prepared to focus on experimental verification of process design needed for the second program phase.

Technical Progress Report

Objectives

Objectives for the Quarter were:

- Complete and submit the final NEPA document;
- Complete the distillation to obtain the bottom cut;
- Generate fractions based on molecular types and functionalities using separation techniques;
- Set up GC/MS system and develop operating experience on initial sample;
- Extend Z-BASIC methodology for other thermodynamic properties such as enthalpies and entropies of adsorption and vaporization;
- Complete subcontracts and initiate marketing tasks by Sinor and Zharadnik;
- Continue marketing efforts and complete testing agreements, where possible, for evaluation of shale oil derived specialty chemicals;
- Continue work on market database and make entries as available;
- Complete subcontract with the University of Utah and initiate work under that subcontract;
- Continue dialogue with LLNL consortium.

Accomplishments

The aforementioned objectives were all met during the quarter with the following highlighting the quarter's efforts.

1. High quality distillations were completed on gallon quantities of shale oil. These fractions will form the basis for study for the remainder of the Phase-I (base period) program.
2. The gc-ms system was specified, ordered, delivered and set up. Algorithms and programs to utilize Z-BASIC for interpretation of gc-ms data have been developed.
3. All proposed subcontracts are in place (subject to ratification by DOE) and work is progressing.

4. Initial screening of extraction solvents have revealed promising solvent system for both $<200^{\circ}\text{C}$ and $200\text{-}275^{\circ}\text{C}$ fractions.

Discussion

Task 1. Task Manager, P. A. V. Devineni

The status of Task 1 has not changed and no additional work was conducted in the present quarter. JWBA is still waiting to hear comments or approval from DOE regarding final submission of the NEPA report.

Task 2. Task Manager, D. E. Cogswell; Assistant, J. W. Wisner

During this quarter, the main emphasis has been placed on:

- (a) Completing the distillation of the atmospheric residual fraction at the University of Utah;
- (b) Selection and screening of solvent systems for liquid-liquid extraction of shale oil fractions;
- (c) Preliminary analysis of data from shake tests using a newly-designed partition coefficient model;

The distillation of ten gallons of the $+275^{\circ}\text{C}$ fraction into $275\text{-}400^{\circ}\text{C}$ and 400°C fractions has been completed at the University of Utah facilities. A thin film distillation apparatus was used to conduct the distillation. These distillation fractions are now being analyzed for their properties and elemental analysis. The final distillation flow diagram with normalized mass balances is shown in Figure-1.

One task emphasis during this quarter has been placed on screening of a solvent matrix for the purpose of liquid-liquid extraction of shale oil fractions. The criteria for solvent selection is based on process selectivity and solvent availability, cost, recovery and handling. Various solvents were considered covering wide spectrum of solvent types that are commonly practiced and believed to be effective from a thermodynamic consideration. Table 1 shows the solvent systems considered.

Table 1. Solvent Matrix

Solvent Type	Solvent Systems
1. Mineral Acids	H ₂ SO ₄
2. Mineral Bases	NaOH
3. Organic Acids	Acetic Acid
4. Organic Bases	Isopropylamine
5. Polar Hydrocarbon	N-methyl-2-pyrrolidone, Furfural, Phenol, MeOH, Isopropanol
6. Non-polar Hydrocarbon	Pentane
7. Antisolvent	Water

Shake tests have been conducted with <200°C and 200-275°C distillate fractions of shale oil using various solvent systems and solvent loadings. The effectiveness of solvent systems are measured in terms of partition selectivity to the desired compound types. Initially, we are concentrating on nitrogen types, but eventually we will also incorporate consideration of valuable oxygen types. The shake-test results will be used to simulate continuous counter-current liquid-liquid extraction operation and to rank various solvent systems. This work is a requisite to Task 5.

For purposes of screening, we initially conduct test-tube experiments observing whether or not phase separation occurs and what the relative volumes of the phases are in relation to the volume of oil and solvent added. For those systems showing promise, a series of larger scale "shake tests" using separatory funnels are completed. Samples recovered from the shake tests are subjected to simple analysis (density, elemental composition, etc.) to assess relative selectivity.

Qualitative observations show that acid extractions are more selective than bases. Neutral water extracted nearly as much as bases. Back extraction of the water with pentane and evaporation of pentane left a brown residue with a wet tobacco odor (nicotinic acid?).

Polar solvent extractions with a little water as an antisolvent were very effective in phase separations. Solvent loadings, from .25 to 2, have been tested for the variable study. Selected extract and raffinate samples are now being analyzed for elemental composition. Ultimately, the most attractive solvent systems will be utilized for continuous liquid-liquid extraction runs.

Mass balance data from shake tests are being used to test the partition model (described in task 3). The objective is to find the distribution of the partition function which would be useful to select the best solvent system and operating conditions.

Task 3. Task Manager, D. E. Cogswell; Assistants: C. P. Russell, P. A. V. Devineni

The development of analytical methodologies is on schedule. Three methodologies related to obtaining thermodynamic properties from gas chromatographic runs are illustrated below:

1. ΔH , ΔS , C_p from GC Runs

The objective of this methodology is to obtain thermodynamic properties such as enthalpy, entropy and heat capacities for components of a given GC peak. From thermodynamic properties, a host of other physical properties can, in principle, be calculated or estimated. Additionally, knowing the thermodynamic properties greatly assists the structural interpretation using Z-BASIC correlations.

The thermodynamic properties of adsorption and solution depend upon the column configuration i.e either packed or capillary column.

Basic equations governing the methodology are:

$$t_r = t_o \left(1 + \frac{k}{v^*} \right)$$

where	t_r	retention time
	k	partition coefficient
	t_o	retention time of non-adsorbing specie
	v^*	ratio of void volume to stationary phase volume in packed column

For a capillary column

$$v^* = \frac{r (1 - \tau_s/r)}{2\tau_s (1 - \tau_s/2r)}$$

where	r	radius of the column
	τ_s	thickness of the stationary phase

This method of solving for thermodynamic properties differs from conventional analysis which is limited to retention times from isothermal operation. Partition coefficient 'k' values are calculated from retention times of temperature programmed runs. The number of runs is proportional to the number of properties to be determined. The solution to the simultaneous equations of properties is obtained by applying a Newton-Raphson technique.

The development of methodology in this quarter included fortran program development and debugging. The program's features consist of:

- (a) calculation of retention times for a given ΔH , ΔS and C_p data and temperature program;
- (b) solution for ΔH , ΔS and C_p given retention times for either isothermal or temperature programmed runs.

Future developmental work will involve testing with actual data. The ultimate purpose of this methodology is to integrate this program with the Z-BASIC program and use it in conjunction with GC-MS system to help resolve peak identification and analysis.

2. Prediction of ΔH_{vap} and ΔS_{vap} for Z-BASIC Methodology

The purpose of this method is to calculate Z-BASIC structural parameters 'r' and 'i' for constant 'n' and 'z' to narrow structural possibilities. The value for the 'i' parameter is the difference in entropy between parent and isomers of the same molecule whereas 'r' is obtained from difference in enthalpies.

The methodology involves the following steps:

- (a) literature search for data on thermodynamic properties for homologous series;
- (b) conversion of data from reference conditions to the desired operating conditions;
- (c) correlation of properties with carbon number 'n' and 'z'.

Progress made includes:

- (a) data collection for z-series of alkanes, alkenes, cycloparaffins, alkynes, alkylbenzenes and alkylnaphthalenes;
- (b) a fortran program has been written and debugged for the calculation of enthalpy and entropy of vaporization at standard reference state for normal and branched paraffins given boiling point and enthalpies at two temperatures;

Preliminary analysis of results for normal and branched paraffins and alkyl substituents indicates that the relationship between difference of enthalpies and length of carbon chain is non-linear. Thus, the applicability of group-additivity approach for treatment of isomeric variations is not practical. The effect of location of methyl group substitution on carbon number is shown in Figures 2 to 4.

In conclusion, present data treatment for 'r' and 'i' is very promising for paraffins and the concept is still evolving. However, as more data become available for other

compound types, it may be necessary to modify or refine definitions for 'r' and 'i'. It is theoretically possible to replace enthalpy and entropy of vaporization with corresponding adsorption values to utilize experimentally measured values as described in the previous section. Further progress is contemplated with experience and knowledge gained in the data treatment.

3. Distribution of Partition coefficients

The partition coefficient, by definition, is a measure of efficiency of separation for separation processes. It is specific to compound types and solvent systems. For a liquid-liquid extraction system, the distribution of partition coefficient is important for simulation of actual operation from bench-scale experiments.

To apply this method, mass balance data are required for various solvent loadings. Different data sets for different solvent types will be needed to find the best solvent system for any shale oil fraction. GC-MS analysis of these fractions will be used for boiling point and molecular weight distribution.

From experimental data, the following parameters are defined:

$$C_s = \frac{\text{Total Moles in Extract}}{\text{Total Moles in Raffinate}}$$

$$R_s = \frac{\text{Moles of Oil in Raffinate}}{\text{Total Moles of Oil}}$$

The partition coefficient 'k' is then related to C_s and R_s as shown in the following equation:

$$R_s = \frac{\int_0^{\infty} \frac{FdK}{1 + C_s K}}{\int_0^{\infty} FdK}$$

The distribution of partition function is given by the equation:

$$F = K^d e^{-(ak^3 + bk^2 + ck)}$$

The solution of this equation requires at least four data points, i. e., four solvent loadings. The distribution of partition coefficient is analogous to the boiling point distribution in a simulated distillation. Even though specific determination of partition coefficient is not measured, the range of partition coefficient values for certain compound types can be experimentally verifiable.

During this quarter, program development has been completed and program analysis is being carried out. Actual data will be tested in the next quarter.

Task 4. Task Manager, P. A. V. Devineni; Subcontractors: J. S. Sinor and R. Zahradnik

Specific goals for the marketing task have been accomplished including:

- (a) Gathering product specifications data and development of a specifications routine;
- (b) Conducting company profiles database search by SIC to develop a preliminary list of potential partners in the shale oil project;
- (c) Initiation of Sinor and Zahradnik marketing subcontracts;
- (d) Organizing a few companies to test shale oil and its derived fractions for activity testing;

Development of product specifications database is very critical to the marketability of shale oil products. Numerous companies have been contacted to obtain product specifications information. Often, supplier's product specifications are slightly different from the standard in order to gain a competitive advantage. Thus it is required that the database have multiple specifications for the same product depending on the source/supplier.

The product specifications database routine has approximately 50 fields to cover the entire spectrum of specifications from CAS number to composition. At present there are 25 products in the database for which specifications are available from at least one commercial source. A typical product specifications output sheet is shown in Table 2. The fields with no specification values illustrate that not all vendors supply complete data and illustrate the complexity in matching production specification with vendor requirements. This database file is amenable to further modifications as deemed necessary.

Another part of the database development includes routines for manipulation of historical supply, demand and price data to project growth patterns. Basic data retrieval and recasting is completed. Program features include data retrieval for previous years and annual data for all states. This routine is specially used to integrate subcontractor data input and evaluation.

Company profiles database from DIALOG has been searched by SIC of target chemicals and product types. The main purpose for the compilation of the list is to obtain potential candidate companies for commercialization venture of shale oil project. From this list, it is intended to narrow down the list to a manageable size for first round contact.

Table 2

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SPX DataBase System

AROMATIC OIL

Formula:	Type:Aromatic Oil	Class:101	CAS:
MW:	BP C-IBP: 350.0	50%: 487.0	EP: 596.0
API: 9.1	Den. gm/cc: 1.0060	Lbs/Gal: 8.38	
RI @20 C: 1.572		V.P atm:	
Flash Pt. C:256.0		Pour Pt. C: 21.0	
Freez Pt. C:		Melt Pt. C:	
Aniln Pt. C: 42.0		Color:	
Vis. cp:	Cst 40C: 968.9	Cst 100C: 24.5	
SUS 100F: 5563.0		SUS 210F: 122.7	
Water %:		Assay :	
Acid #:	Base #:	Neutral #: 0.20	

Elemental Analysis

C %:
H %:
N %:
S %: 4.36
O %: (dif)

Molecular Type

Saturates %:16.20
Aromatics %:73.20
Polars %:10.60
Asphaltene %:
Resid:
Misc.:

Carbon Type

CN %: 13.00
CP %: 49.00
CA %: 39.00
Ash%:
Solubility:

Source: exxon-111

The list of SIC numbers with product categories is given in Table 3.

Table 3

SIC	Product Type Search	# of Potential Companies
2833	Chemical Manufacturing/Medicinal and Botanical	96
2821	Plastic Resins	84
5169	Chemical Products NEC(Misc.)	97
5169	Resins, Chemical products	5
2992	Lubricating Oil	200
2911	Petroleum and Coal products	23
3624	Carbon Products	35
5172	Petroleum Products NEC Oils	21
2899	Chemical Preparations (NEC) Oils	25
2911	Petroleum Refining	235
2834	Pharmaceutical Preparations NEC	66
2843	Surface Active Agents	32
2865	Cyclic crudes and Intermediates	82
2869	Amines, Acids & Esters	6
2879	Agricultural Chemicals	71
2869	Fragrance Chemicals	4
2865	Tar Products	4

The difference between this list and the previously reported list (refer to Quarterly Report 1) is that for the current list, complete company profile information is available including possible contacts. The latest petrochemical directories and other database sources have been used in compiling the information. This list has been submitted to Dr. Zahradnik for his recommendations and screening.

Marketing subcontracts with Mountain Bay Associates (Dr. Zahradnik) and J. E. Sinor Consultants (J. E. Sinor) are in place. Work statements have been agreed upon and work is in progress. As part of the subcontract, Mr. Sinor would take a detailed look at the target chemicals from shale oil and compile this data. Dr. Zahradnik is assisting the project in identifying potential companies and establishing contacts to promote the shale oil project and its value added chemicals.

JWBA is making arrangements with a few chemical companies that are involved in agricultural and pharmaceutical intermediates to test the activity of shale oil and its fractions. This activity testing would involve both biological and toxicity testing. The importance of this area of research is that for the first time shale oil will be evaluated for biological activity, thus taking advantage of the heterocyclic functional groups. Applications would be in fungicides, biocides and pharmaceutical industries. This work is expected to accelerate the product development schedule.

Task 5. Task Manager, J. W. Bunger; Assistant, D. E. Cogswell

In managing the separations tasks, it became apparent that some separation optimization at this stage would pay off in the end. During our prior work, we had identified certain systems which were acceptable from an operational standpoint but which were not necessarily optimal. Two considerations now must be accounted for. First, we now know that the extremely valuable components, i.e., >\$100/bbl, and that are present in appreciable concentrations in shale oil, will likely be nitrogen compounds. Therefore, one simple objective is to optimize the separation of nitrogen compounds from non-nitrogen compounds.

Second, it becomes important that the systems selected promise reasonable commercial viability; one objective of the program being to develop the data needed to interest the private sector in the profit potential of pursuing subsequent development. The Separations Exploration Task is designed to address both of these requirements. Upon review of the schedules and objectives, it appeared fruitful to engage in initial screening activities prior to completion of Task 2. By this approach, we help ensure that the samples we analyze, even at the initial characterization stage, are a step closer to the concentrates producible commercially.

In our screening work, we have adopted a simple method to assist in our screening defining a parameter known as a coefficient-of-separation (CS). The coefficient-of-separation is a parameter commonly used in the extractive metallurgy industry and represents the degree to which an ideal separation of the target product is made. There are several definitions but the simplest one for our purposes is:

$$CS = \%N - \% \text{ non-N}$$

where % N is the mole percent of all nitrogen compounds which are concentrated in the extract.

 % non-N is the mole percent of all non-nitrogen compounds which are concentrated in the extract.

This definition accounts both for the % recovery (the first item) but also penalizes the quality of separation if a lot of non-nitrogen compounds are extracted as well. It is believed that for a given system that the coefficient of separation will be roughly correlatable with economics.

To illustrate, consider the data in Table 4 which are actual data for a polar/non-polar extraction using differing oil/solvent ratios. As the solvent ratio goes up, the amount of extract goes up and so does the % N recovery. However, the amount of non-nitrogen compounds extracted also goes up and the CS goes down. By this data, the maximum recovery of nitrogen for the least inclusion of non-nitrogen compounds occurs at an oil/solvent ratio of 1.0.

In the Exploratory Separations Task, all samples will be treated similarly. Separation of oxygen compounds will also be evaluated by this approach. The most attractive systems and oil/solvent ratios will be subjected to continuous counter-current extraction.

Table 4
Illustration of Selectivity Criteria
% N in feed = 0.53 (8.33 mole % nitrogen compounds)

Oil/Solvent (single stage)	Fraction (% of feed)*	% N	% N Recovery	CS
1.68	R(67)	.25	68	35
	E(33)	1.09		
1.00	R(67)	.09	87	60
	E(33)	1.40		
0.50	R(47)	.07	94	44
	E(53)	0.94		
0.33	R(41)	.04	98	42
	E(59)	.88		
0.25	R(19)	.03	99	20
	E(81)	.65		
	*E =	Extract		
	R =	Raffinate		

Objectives for the Next Quarter

- Generate data on gc/ms extraction samples and find prominent target chemicals in the chromatograms;
- Generate an initial batch of 25 samples for activity testing by major chemical companies;
- Finalize the methodology and program development for marketing data base and conduct test runs;
- Continue efforts to market shale oil project to potential companies;

- Present results at METC Contractors Meeting and Eastern Oil Shale Symposium;
- Conduct exploratory continuous liquid-liquid extractions and analyze results;
- Conduct exploratory studies of hydrodealkylation to product low molecular weight nitrogen compounds.

Figure 1: Shale Oil Distillation

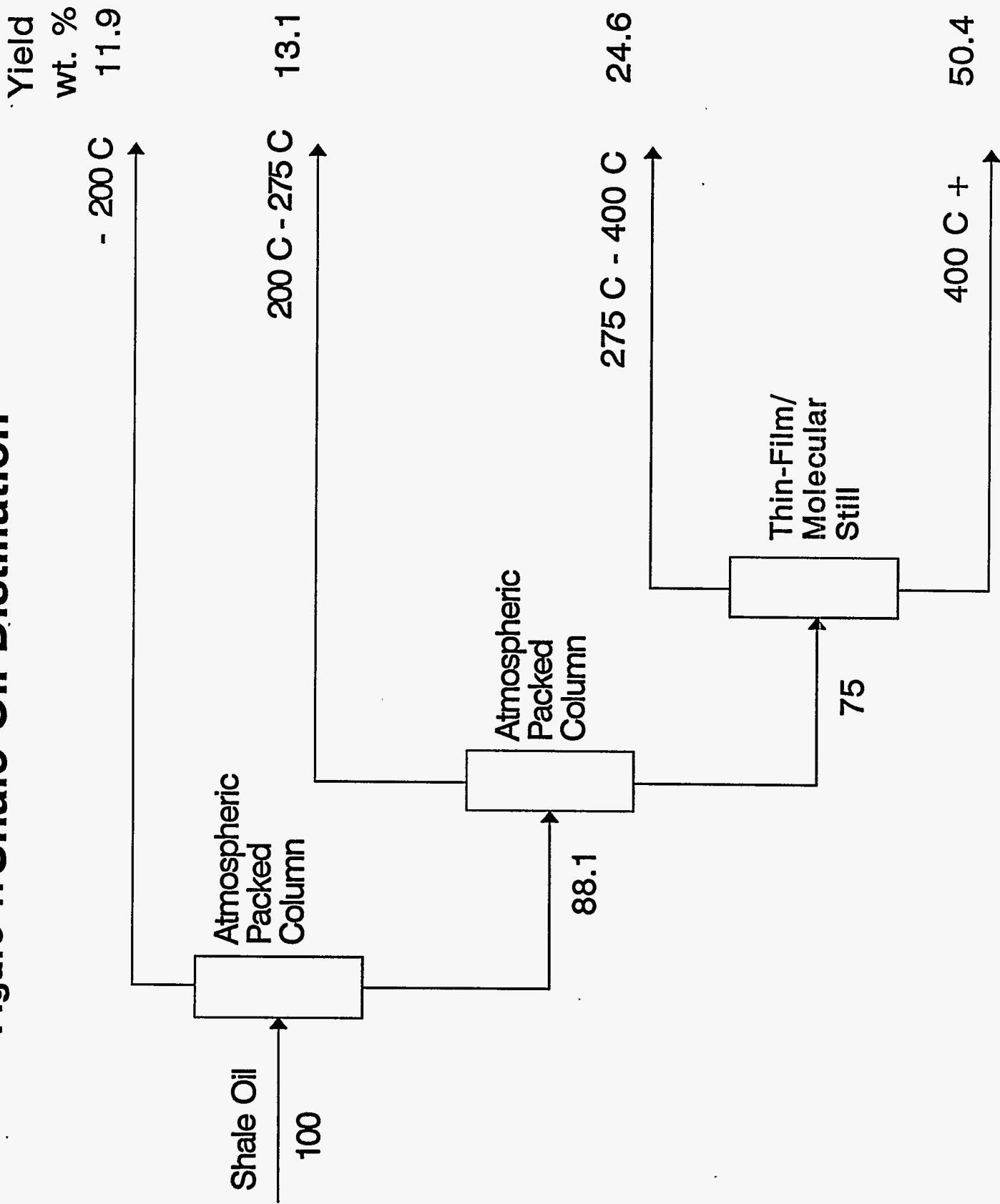


Figure 2: Effect of Branching on ΔH_v^0
(Position of Methyl Group)

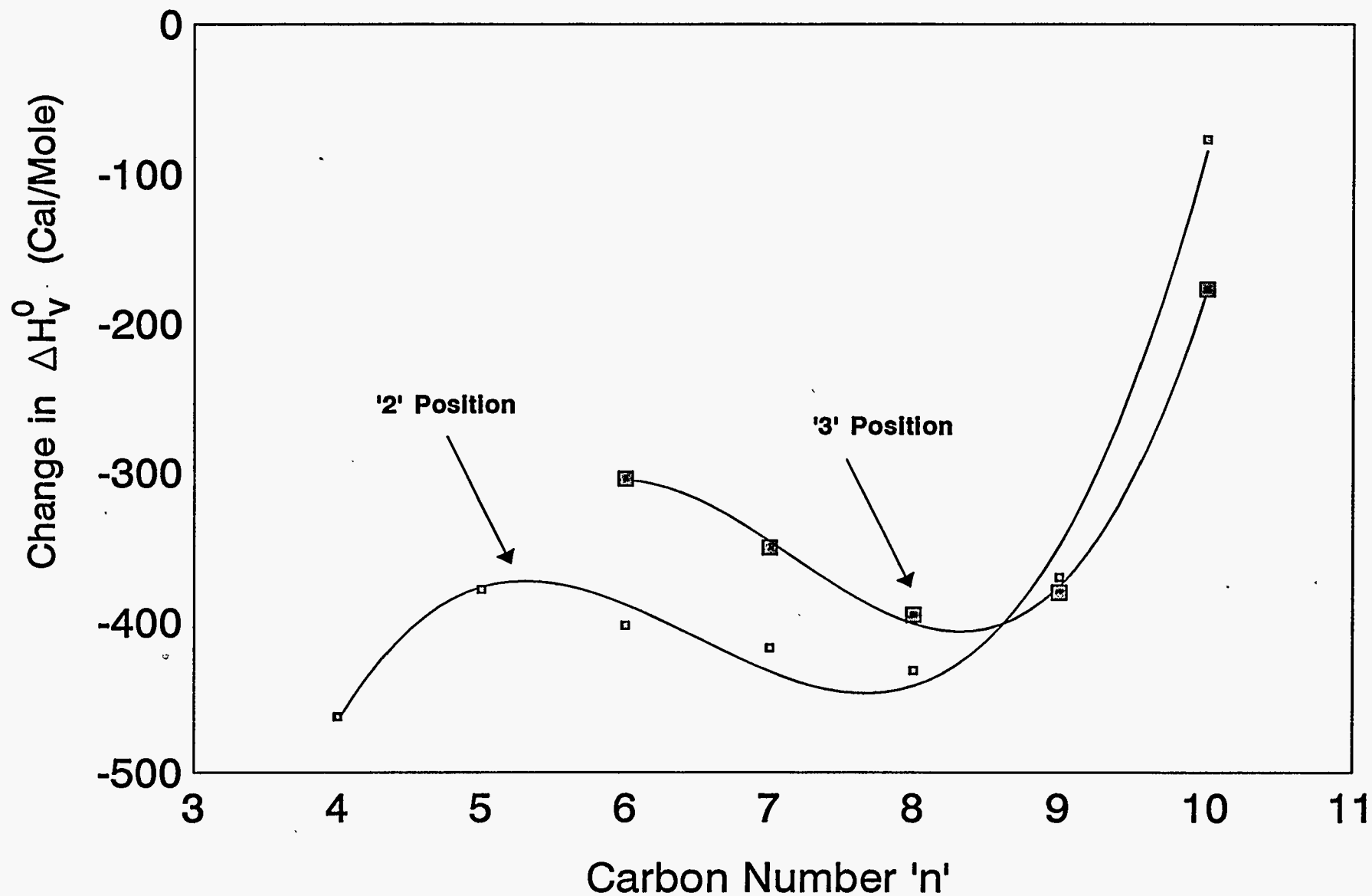


Figure 3: Effect of Branching on ΔH_V^0
(Position of Dimethyl Group)

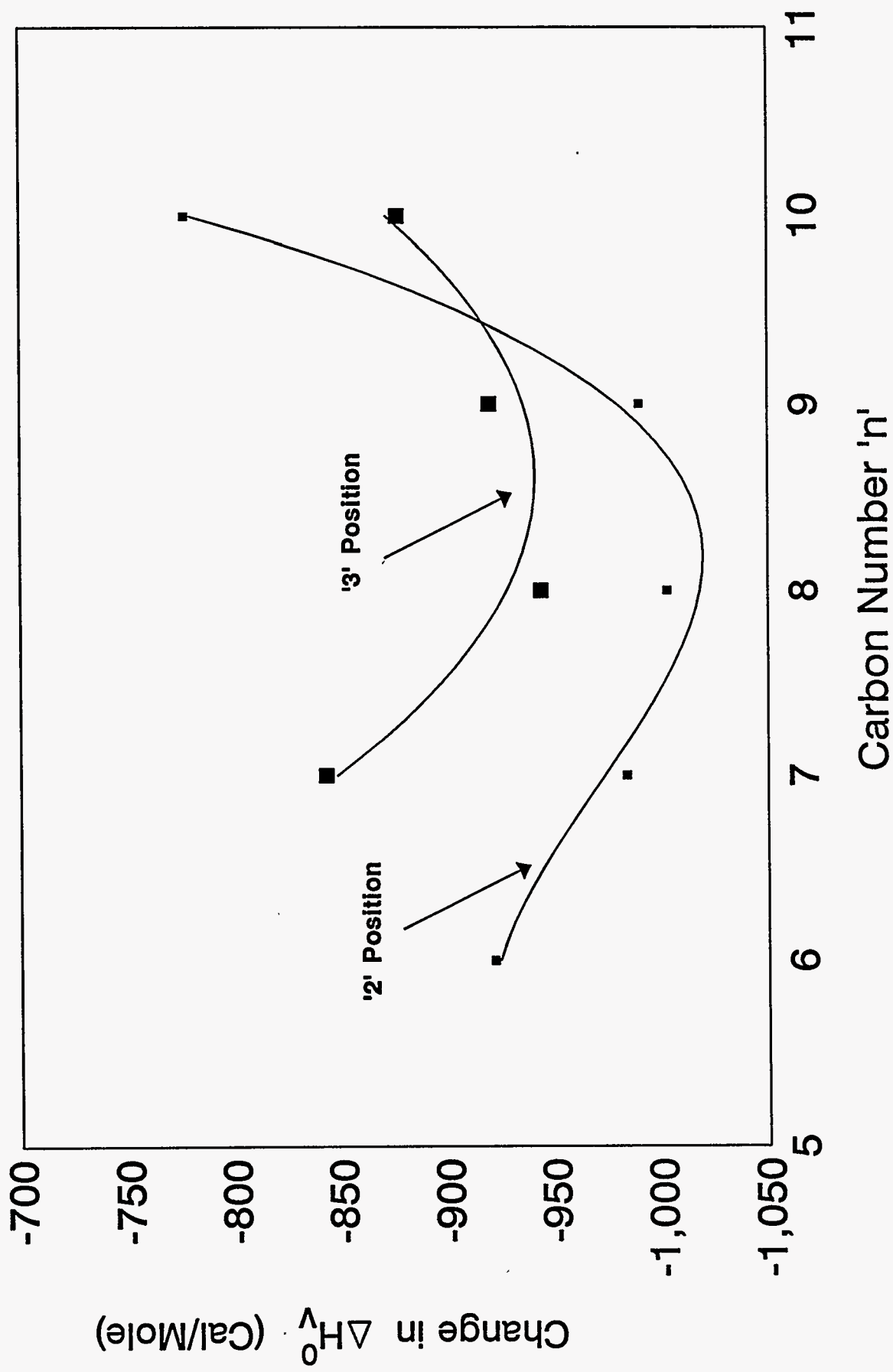


Figure 4: Effect of Adding a Carbon on ΔH_V^0

