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## Previous Conferences

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2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, USA, July 29-August 1, 1986. Proceedings published by the Southwest Research Institute, Leo L. Stavinoha, editor; San Antonio, Texas, USA, October 1986.

3rd International Conference on Stability and Handling of Liquid Fuels, London, England, September 13-16, 1988. Proceedings published by the Institute of Petroleum (London), R. W. Hiley, R. E. Penfold, and J. F. Pedley, editors; London, England, November 1988.

4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, USA, November 19-22, 1991. Proceedings published by the U. S. Department of Energy, Harry N. Giles, editor; Washington, DC, USA, 1992.

5th International Conference on Stability and Handling of Liquid Fuels, Rotterdam, the Netherlands, October 3-7, 1994. Proceedings published by the U. S. Department of Energy, Harry N. Giles, editor; Washington, DC, USA, 1995.

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## Preface

The association's international conferences continue to be the premier forum for papers on stability and handling of liquid fuels, and attract the world's leading authorities on these topics. The 170 delegates from 24 countries on all five continents who attended IASH '97, the 6th of these conferences, attest to their importance.

Within the North America and much of Europe, legislative initiatives and an enlightened environmental awareness have resulted in stringent product specifications and stricter practices at fuel handling and storage facilities. In the U. S., for example, gasoline marketed in certain ozone nonattainment areas is required to contain at least 2 percent oxygen, and less benzene and other aromatics than previously allowed. By the year 2000, the entire U.S. gasoline pool may be reformulated. In many countries, diesel fuel must have an ultra-low sulfur content, and it is possible that even home heating oil may eventually have to conform to this new standard. Stringent product specifications and environmental and statutory requirements are compelling refineries to upgrade their processes to produce cleaner burner fuels.

In the U.S., some refineries have been shutdown rather than investment made in their upgrading. Although reformulated fuels have been in the marketplace for several years now, we still do not fully know how some of them will withstand the rigors of handling and storage, or stand up to microbial attack. Complicating the need to produce cleaner fuels, the world crude oil stream is getting heavier and higher in sulfur. More severe processing is necessary, therefore, to obtain specification products. Moreover, there is a greater tendency to upgrade the bottom of the barrel to provide more transportation fuels in response to rapid growth in demand. These trends are exacerbating problems with product quality and stability.

Despite the dramatic changes in the composition of the gasoline and diesel fuel pools and the relative sparsity of data on their stability, papers on aviation fuels dominated this conference as they did at the 5th conference in Rotterdam. Hopefully, the 7th conference in the year 2000 will have more papers on handling and environmentally-friendly fuels.

I thank the following companies and organizations that provided generous financial support for this conference: Angus Chemical Co.; the Arabian Fuels Center; BDM Oklahoma; BetzDearborn Hydrocarbon Process Group; BP/Plasmos; Chevron Products Co.; Emcee Electronics, Inc.; Ethyl Petroleum Additives; the FQS Group, Inc.; ITS-Caleb Brett; Nalco/Exxon Energy Chemicals, L.P.; Octel America; Oiltanking Houston, Inc.; Saybolt Nederland BV; SGS Canada; Varlen Instruments, Inc.; and the U. S. Air Force Wright Laboratory.

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I am also grateful to the many people and organizations that assisted me in organizing this conference. Among them are Ms. Tamika Green of the U. S. Department of Energy, Mrs. Shirley Bradicich and Mrs. Jan Tucker of the Coordinating Research Council, Dr. Edmund W. White, consultant, and Ms. Erna J. Beal of the Naval Research Laboratory. The Canadian Embassy in Washington, DC and Tourism *Vancouver* provided support and assistance in bringing this conference to Vancouver. Finally, I thank everyone that attended the conference. Their interest and support ultimately make these conferences successful.

In opening the 4th conference in Orlando, FL, I reminded the delegates of the words of Francis Bacon, founder of the scientific method, that "science makes books, not books science." I have noted that Powertech Labs. Inc., employer of one of the opening keynote speakers, includes another quote from Bacon in its literature, namely "knowledge is power." I am confident the knowledge gained at the 6th conference will help power our quest for a better understanding of fuel instability and improved handling practices.

Harry N. Giles  
Conference Chairman



*6th International Conference on  
Stability and Handling of Liquid Fuels*  
Vancouver, B.C., Canada  
October 13-17, 1997

**CONTROLLING RESIDUAL MARINE FUEL COMPOSITION BY TGA**

John D. Bacha

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**ABSTRACT**

Residual fuel oils are produced by blending cutter stocks with petroleum residues. Petroleum refiners' increasing adeptness at converting more of the bottom-of-the-barrel to light products can/does affect the quality of the derivative oils. All residual fuel oils exhibit some bimodal character, reflecting the volatilities and other characteristics of the light and heavy components from which they were generated. Residual fuels produced from some solvent-extracted residues can exhibit extreme bimodal character (dumbbell blends). While such fuels may meet existing standard specifications, they have been found to readily foul injectors of large marine diesel engines. The compositional deficiencies of such fuels can be characterized, monitored and controlled by use of thermal gravimetric analyses.

**INTRODUCTION**

Heavy fuel oil is a traditional outlet for the heaviest portions of a barrel of petroleum (crude oil). Many heavy fuel oils are simple blends of petroleum resids (distillation residues) and cutter stock. The latter serves to cut (reduce) the viscosity and density of the resids and otherwise render them suitable for use as fuel in large marine diesel engines and other power generating applications.

Petroleum and virgin (straight run) resids are composed of a continuum of hydrocarbon and heteroatomic molecular species which can be classified variously. For certain applications, it is useful to divide the range of constituents into a series of solubility classes, e.g., oils, resins and asphaltenes. By one commonly accepted scheme,<sup>1</sup> oils are propane-soluble constituents; resins are insoluble in propane, but soluble in pentane; and asphaltenes are insoluble in propane and pentane, but soluble in toluene. Analyses reveal important discerning features of the solubility classes across the series, e.g., molecular weight, aromaticity and heteroatom content increase, while hydrogen content declines.

Virgin petroleum resids are naturally stable. Solubility of even the least-soluble species is maintained by the continuum of species present. In this regard, the resins are thought to function as peptizing agents which facilitate the dissolution of asphaltenes in the oil phase.

Over the years refiners have devised a variety of innovative processes to wring more high-value light products from the heaviest portion of a barrel of petroleum. Included are: solvent extraction, visbreaking and thermal cracking. As a result, the natural blend of oils, resins and asphaltenes in virgin resids becomes more or less severely altered. How severely a resid is altered influences the ease with which it can be incorporated into heavy fuel oils with adequate stability and performance characteristics.

Given the relative values of petroleum resids, cutter stocks and finished heavy fuel oils, economics dictate minimization of heavy fuel oil production and cutter usage. It is logical for blenders to use the minimum quantity of the lightest cutter that yields an acceptable fuel oil. It follows that the majority of modern heavy fuel oils to some degree or other are composed of a bimodal distribution of light and heavy components. Our experience is that extreme bimodal distribution is a critical feature of heavy marine diesel fuel oils which readily foul fuel injectors; this compositional deficiency is linked to the nature of certain processed vacuum resids from which the problem fuels are produced.

## **RESULTS AND DISCUSSION**

The simplest heavy fuel oils are blends of virgin atmospheric or vacuum resids and cutter (Figure 1). Since most modern petroleum refineries are equipped with vacuum distillation units, production of heavy fuel oil from atmospheric resids is rare. Vacuum distillation is part of the primary mechanism used by petroleum refiners to increase the volume of high-value light products from a barrel of crude oil. In a typical case, vacuum distillation splits an atmospheric resid (750°F+), which can constitute up to 40 volume percent of a crude oil, into about equal volumes of vacuum gas oil (750-1000°F) and vacuum resid (1000°F+). The vacuum gas oil so generated is used as cracker feedstock and thereby converted to additional light products.

More complex heavy fuel oils are generated from processed vacuum resids. As noted earlier, processing of vacuum resid can affect the performance characteristics of heavy fuel oils derived therefrom.

Solvent extraction is among the processes used by refiners to generate additional light products from vacuum resid. The succession of solvent extraction processes that have been developed differ primarily in the extraction solvent used, i.e., propane, butanes or pentanes (Figure 2). The extraction processes remove asphaltene-free oils for use as cracker feed, leaving behind asphaltene-rich tars that are often disposed of by incorporation into heavy fuel oils.

As indicated by the classic work of Mitchell and Speight,<sup>2</sup> the series of extraction solvents (propane, butanes and pentanes) can be expected to be increasingly aggressive in extracting the lighter (lower molecular weight) constituents of a vacuum resid (Figure 3). As more lighter constituents are removed, the residual tar can be expected to become heavier.

When propane is used as the extractant, the typical yield of extracted oils is about 50%. The residual tar is composed of the heaviest oils, the resins and the asphaltenes. Although the natural blend of vacuum resid constituents is physically altered by removing most of the heavy oils, the molecular features of the remaining constituents remain intact. The latter distinguishes extraction processes from more severe thermal conversion (cracking) processes.

When butanes and pentanes are used to extract heavy oils from a vacuum resid, the typical yields of extracted oils are about 70% and 85%, respectively; the residual tars are proportionally heavier and more viscous. When pentanes are used, the residual tar consists entirely of asphaltenes (by definition). In practice, when pentanes are used, some portion of hot cutter must be introduced into the process upstream of the steam stripper to prevent deposition of heavy tar (asphaltenes) in the process equipment.

Our experience is that heavy fuel oils produced by simple blending of light cutter and vacuum resid that have been extracted with butanes or pentanes are not suitable as such to power most marine diesel engines. While such fuels may meet an existing set of specifications, they are prone to foul fuel injectors on attempted use. In the worst case situations, the result is formation of massive cauliflower-like carbonaceous deposits on the fuel injectors, with consequent poor fuel atomization and eventual engine stoppage.

Selected properties of such a problem fuel (Fuel A) are shown in Figure 4. While this fuel meets most of the specification requirements of all three grades of heavy marine diesel fuel listed, high density and high carbon residue force it into the lowest grade, Grade RMK 35.

Further investigation unlocked other deficiencies. What we believe is a critical compositional deficiency, extreme bimodality, was elucidated by thermal gravimetric analysis (TGA).

The primary curve of a flow TGA of a sample of Fuel A (Figure 5) shows the weight loss of the sample as it was heated from ambient to 550°C under nitrogen flow, and then to 900°C after introduction of air at 550°C. The first derivative (DTGA) curve, which indicates the rate of change in weight loss, shows three major peaks. The first peak can be associated with simple evolution of volatile components (distillation), while the second peak represents the evolution of cracked species (destructive distillation). The third peak is due to burn-off of deposited carbon (coke) and can be used as an approximate measure of carbon residue (see Figure 4).

We believe that the deep valley between the first and second peaks of the first derivative curve is particularly instructive. We believe it graphically illustrates the compositional deficiency of the problem fuel, i.e., the absence of a continuum of volatile species which can effectively sustain fuel fluidity during injection. In most instances, the end result on attempted use is formation of carbonaceous injector deposits from the heaviest components in the fuel.

While flow TGA provides a broad look at certain characteristics of a fuel (distillation, cracking and carbon burn-off), vacuum TGA provides a more-focused look at the distillation portion (Figure 6). Numerical values derived from the vacuum TGA (Figure 7) are useful for further demonstrating the paucity of intermediate volatility components which we would argue provide the continuum of volatile species needed for effective fuel injection, atomization and combustion.

Our experience is that potential problem fuels derived from certain extracted vacuum resids can be corrected by further blending with suitable heavy hydrocarbon, e.g., heavy gas oil, virgin atmospheric or vacuum resid, or another heavy fuel oil generated from non-extracted resid. The flow TGA of such a fuel (Fuel B), which was produced by blending a potential problem fuel with another heavy fuel oil generated from non-extracted vacuum resid, is shown in Figure 8. As illustrated, the added material serves to fill the gap in the continuum of volatile species we believe is needed for good performance. Comparison of vacuum TGA numerical values for Fuels A and B (Figure 7) indicates how the distribution of components was altered. Experience suggests that a minimum of about 30% 650-1000°F boiling range material is needed to obviate

performance problems. More familiar properties of Fuel B (Figure 4) show that it qualifies as the best of the three fuel grades listed, Grade RMG 35.

Commercial experience indicates that far-less heavy hydrocarbon is needed to correct a potential problem fuel than is generated by the extraction process that spawned the potential problem fuel. Thus, operation of the extraction process is still economical. In most instances, back-blending with heavy hydrocarbon also serves to reduce the fuel carbon residue value. The latter is important because it is our experience that the combination of lack of a continuum of volatile species and high carbon residue is most characteristic of heavy fuels that are especially prone to foul fuel injectors of heavy marine diesel engines.

## **CONCLUSIONS**

Based on the preceding results and discussion, we conclude that:

- Flow thermal gravimetric analysis is a useful tool for determining the volatiles evolution characteristics and estimating the carbon residue content of heavy fuel oils.
- Flow and vacuum thermal gravimetric analyses together provide a means of identifying potential problem fuels derived from certain extracted vacuum petroleum resids, estimating the magnitude of inherent compositional deficiencies, and confirming correction of the deficiencies detected.

## **REFERENCES**

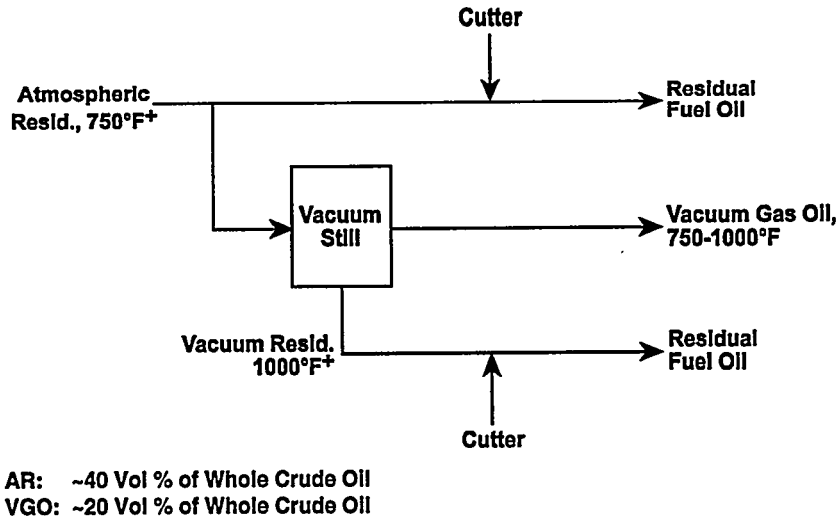
- (1) Speight, J. G., *The Chemistry and Technology of Petroleum*, Marcel Dekker, Inc., 1980.
- (2) Mitchell, D. L. and Speight, J. G., *Fuel*, 52, 149-152 (1973).

## **ACKNOWLEDGMENTS**

The author gratefully acknowledges the laboratory support provided by Russell Polk, Chevron Products Company, Fuels Technology Team, and the critical analytical support provided by Chevron Research and Technology Company, Analytical Sciences Unit members: Fu Su and Russell Fong.

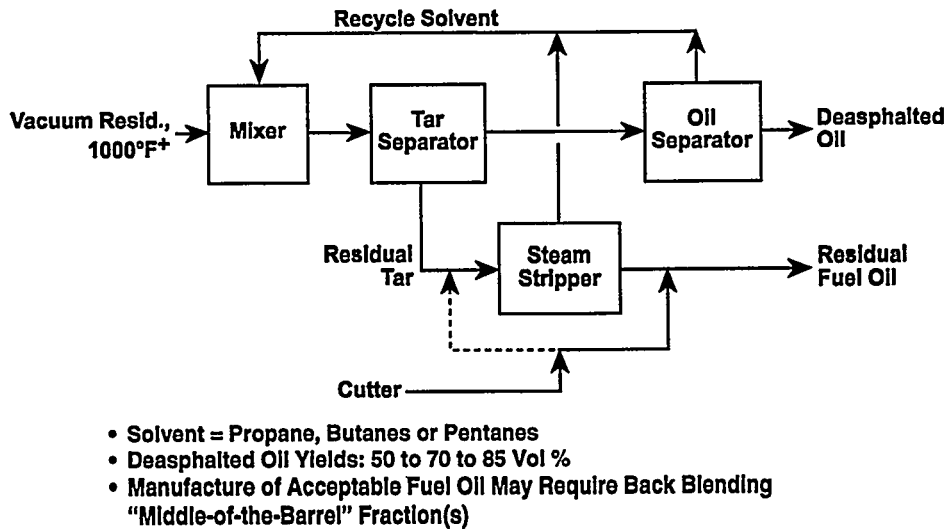
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**Figure 1. Residual Fuel Oils From Straight Run Resids**



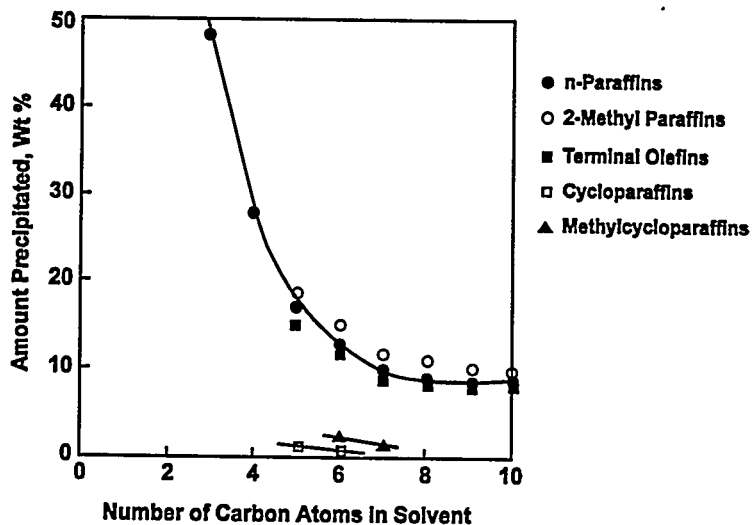
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**Figure 2. Residual Fuel Oils From Solvent Extracted Resids**



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**Figure 3. Precipitate Yields From a Natural Bitumen Using Various Solvent Types**



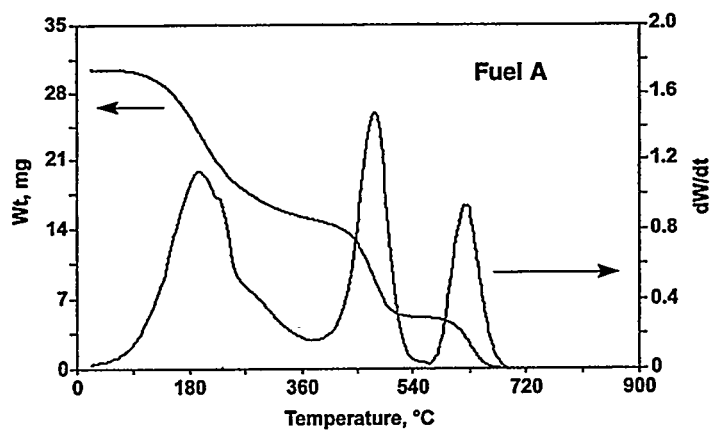
Reference: D.L. Mitchell and J.G. Speight, *Fuel*, 52, 149-152 (1973)

**Figure 4. Residual Fuel Oils Selected Properties and Specifications**

			ASTM D 2069 Marine Fuel Specifications		
	Fuel A	Fuel B	Grade RMG 35	Grade RMH 35	Grade RMK 35
API Gravity, 60°F	10.3	11.2	---	---	---
Density at 15°C, kg/m <sup>3</sup>	997	991	991.0 Max.	991.0 Max.	---
Viscosity at 100°C, cSt	ND	ND	35.0 Max.	35.0 Max.	35.0 Max.
Viscosity at 50°C, cSt	344	374	390 Max.	390 Max.	390 Max.
Flash Point, °C	98	102	60 Min.	60 Min.	60 Min.
Total Sulfur, Mass %	1.7	1.9	5.0 Max.	5.0 Max.	5.0 Max.
Carbon Residue, Mass %	20.6	17.5	18 Max.	22 Max.	22 Max.
Flow TGA Coke, Mass %	16.8	11.7	---	---	---

ND = Not Determined

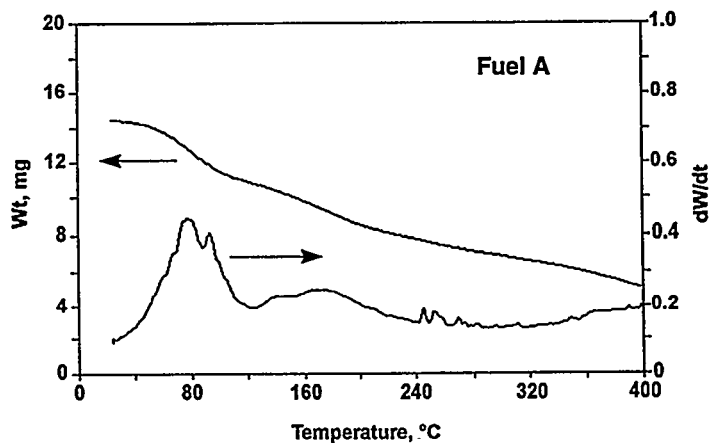
**Figure 5. Thermogravimetric Analysis  
Flow TGA - Fuel A**



- Atmosphere: N<sub>2</sub> to 550°C, Then Air to 900°C
- Flow Rate: 100 cc/Min.
- Heating Rate: 10°C/Min.

08701881

**Figure 6. Thermogravimetric Analysis  
Vacuum TGA - Fuel A**



- Atmosphere: Vacuum
- Heating Rate: 5°C/Min

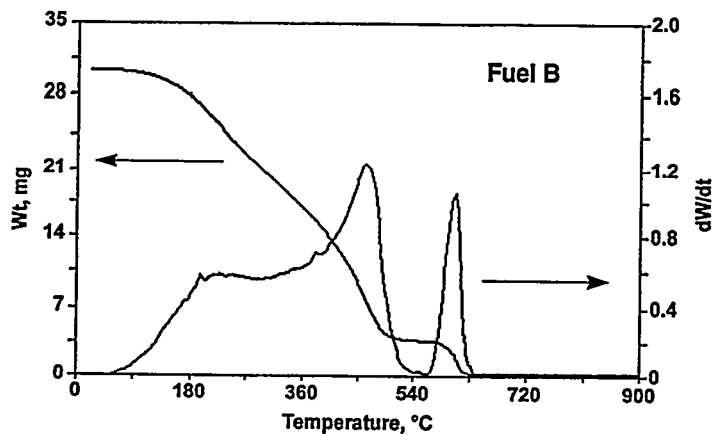
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**Figure 7. Compilation of Vacuum TGA Data  
Percent "Distilled" by VTGA (Simulated Distillation)**

TBP, °F	Fuel A	Fuel B
Below 650	28.2	15.4
650-800	12.4	16.3
800-1000	11.0	22.1
1000-1200	7.8	17.5
Above 1200	40.6	28.7
Below 650	28.2	15.4
650-1000	23.4	38.4
Above 1000	48.4	46.2

**Figure 8. Thermogravimetric Analysis  
Flow TGA - Fuel B**



- Atmosphere: N<sub>2</sub> to 550°C, Then Air to 900°C
- Flow Rate: 100 cc/Min.
- Heating Rate: 10°C/Min.

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**6<sup>th</sup> International Conference  
on Stability and Handling of Liquid Fuels**  
Vancouver, B.C., Canada  
October 13 - 17, 1997

**FUEL BLENDING: HOW TO MINIMIZE RISK OF INCOMPATIBILITY**

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A sound theory for understanding the principals of residual fuel compatibility and stability has been available for decades. "*The Stability of Residual Fuels -Theory and Practice of the Shell Concept*" was presented in some detail at the 16<sup>th</sup> CIMAC Conference in Oslo, in June 1985 by Lewis, Johnson and Berryman. Griffith and Siegmund of Exxon Research presented an equally detailed methodology in their paper "*Controlling Compatibility of Residual Fuels*" which was presented to the ASTM Symposium on Marine Fuels in 1983. I have also found an excellent paper published in 1938 by Hulse and Thwaits of the Standard Oil Development Co. (now Exxon Research and Engineering Co.) on fuel stability and a sediment test procedure which was the forerunner of Exxon's Sediment by Hot Filtration Sediment test. Van Kerkvoort and Nieuwstad published an equally comprehensive paper in 1951 in the J Institute of Petroleum. This paper also discussed the theory of compatibility, and I believe this paper gives the first detailed description of the Shell Hot Filtration Sediment Test. The Shell and Exxon tests evolved into very similar procedures. A careful reading of these papers reveals that the Shell and Exxon theoretical bases for stability and compatibility are in fact very similar. The following discussion is based on the principles espoused in the referenced papers.

A residual fuel oil is a colloidal dispersion of high molecular weight asphaltenes in an oil continuous medium. Although the asphaltene dispersion is frequently referred to as being dissolved in the oil phase (maltenes) it is widely understood to be a colloidal system. The solvent power of the oil phase was referred to as peptizing power ( $P_0$ ) by Shell researchers. The Exxon researchers characterized the oil phase solvency by its solubility parameter. This in turn was related to the Bureau of Mines Correlation Index (BMCI). In my previous paper to the 5<sup>th</sup> International Conference on Stability and Handling of Liquid Fuels I disclosed an algorithm for



The definition for the required aromaticity of the asphaltenes is the minimum proportion of an aromatic solvent in an aromatic/paraffinic solvent mixture which just keeps the fuel asphaltenes dissolved (dispersed). Toluene and heptane are the solvents required for the determination of Toluene Equivalents (TE). We described a simple and rapid titration procedure for determining (bracketing) TE in our previous paper. The solvents required for determination of FR<sub>max</sub> are  $\alpha$  methyl naphthalene (1-MN) and cetane. (Exhibit 3) While Shell does not cite the reason for selecting this pair of solvents, it is interesting to note that 1-MN and cetane are the 0 and 100 cetane reference fuels for determination of cetane number by means of the CFR engine. The solvency rating for these components is just the opposite, i.e., 100 and 0 for 1-MN and cetane respectively. In other words, the best solvent for asphaltenes (1-MN) has the poorest cetane (ignition) quality (0 cetane No.). It has been long known that the highly aromatic decant (or slurry) oils produced in fluid catalytic cracking processes are among the best diluents for residual fuels. These fractions have very poor cetane quality.

The following actual case history illustrates how these techniques are used. Sample 8392 is a commercial IF 380 fuel recently delivered in a major US port. The fuel TE is 60. The first TE run brackets the TE between 67 and 50. A second titration, with varied Toluene/heptane ratios brackets the TE between 63 and 56. (Second titrations are normally only required for fuels with TE >50.) The TE is estimated at 60. (Exhibit 4) While the bracketing method does not yield a "precise" TE, we have found that the accuracy is sufficient for the stability assessment. Based on DNVPS experience, fuels with TE  $\geq$  50 are relatively unusual. The majority of commercial Western Hemisphere fuels are  $\leq$  33 TE. A compatibility test (D 2740?) with MDO A indicated these two components were incompatible. This however does not mean that fuel 8394 cannot produce a compatible blend. A high TE blend component such as fuel 8394 requires great care in the selection of the light blend component. A compatibility test of this fuel with component B confirms that a compatible blend is possible. (Exhibit 5)

An examination of the properties of the two MDO's confirms that MDO A is a significantly more paraffinic distillate (806 CCAI) than MDO B (860 CCAI). (Exhibit 6)

Based on DNVPS experience, we consider fuels with TE > 33 as "sensitive" fuels. The greater the TE, the more sensitive the fuel. The fact that a fuel is sensitive does not mean stable/compatible blends are not possible. Rather, it means that the selection of the blend component is extremely important. In such cases the most aromatic (highest CCAI/lowest cetane Index) MDO's are the best choice as seen in the above example. In addition, the order of mixing of the components is very important. For best results the poorer solvent (higher CCAI component) should be added to the "sensitive" (higher TE) blend component. Slow addition coupled with effective mixing, produces a slow and gradual change in the solvency of the blended fuel. The alternative mixing order, the addition of the sensitive fuel to the poor solvent produces a situation where the initial increments of the "sensitive" fuel are exposed to a large excess of the poor solvent. This is the most unfavorable environment and can lead to agglomeration and precipitation of asphaltenes. Our experience indicates that once the asphaltene colloidal structure is disrupted (agglomeration, precipitation) it is extremely difficult to re-disperse (re-dissolve) the agglomerated asphaltenes.

While not discussed in the present paper, our previous report indicated that the risk of incompatibility when mixing two IFO's is very low to negligible. This is explained by the fact that the majority of commercial IFO's have BMCI's of > 70. Such fuels have sufficient aromaticity to blend with all but the most "sensitive" fuels. Even though the risk of incompatibility is low when mixing IFO's, DNVPS continues to advise customers to avoid or minimize mixing IFO's, mainly because of legal considerations.

IFO blends follow the same rules as MDO/IFO blends. The only IFO's of concern are unusually low CCAI fuels, and then only with the most sensitive IFO's. A simple Go/No go spot test with a 33 TE solution (2/3 heptane 1/3 toluene) can easily identify a "sensitive" blend component. This test is run by adding 10 ml of the 33 TE solution to 1 gm of the sample to be rated. A uniform black spot is a pass, (TE < 33) while a "bulls eye" (No. 5 ASTM spot) spot is a fail (i.e., TE > 33). If the fuel is "sensitive," it will require care in the selection of the MDO component. (Exhibit 7)

## **Future Work.**

**We are currently refining procedures to determine BMCI of MDO's. This work will be reported in a future paper.**



DNV

## Requirement for Stable Fuels/Compatible Blends

$P_o$  / BMCI = Availability Aromaticity of Oil Phase  
(Peptizing Power)

FR max. / TE = Required Aromaticity of Asphaltenes  
(Flocculation Ratio / Toluene Equivalents)

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6th International Conference/Vancouver





## Requirement for Stable Fuels/Compatible Blends

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$$\frac{P_o}{FR \text{ max.}} \geq 1 \quad (\text{Shell})$$

$$\frac{BMCI}{TE} \geq 1.15 \quad (\text{Exxon})$$

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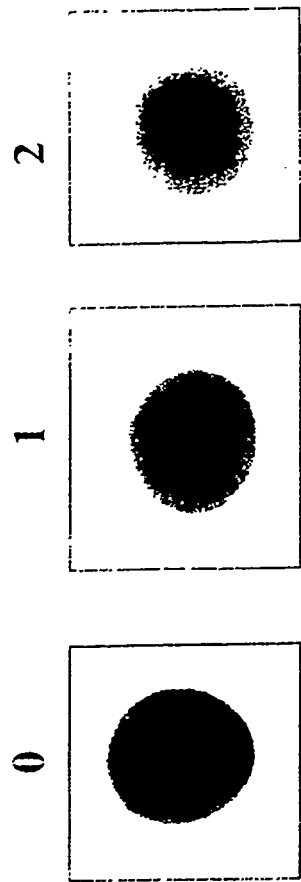
6th International Conference/Vancouver





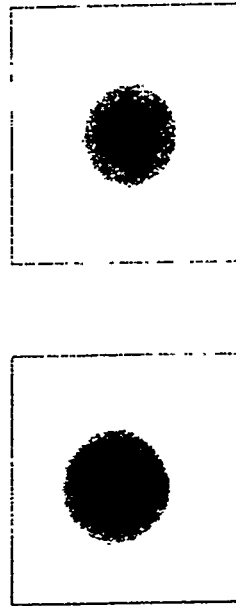
# Toluene Equivalents Test

IFO No. 8392



Heptane  
Increments

TE 100 67 50

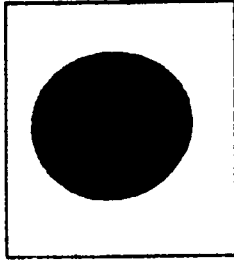


TE

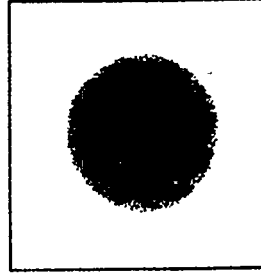


# IFO / MDO BLENDS

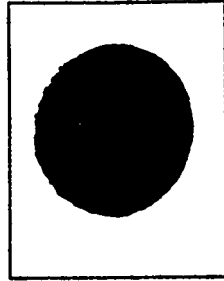
3 hrs @ 80°C



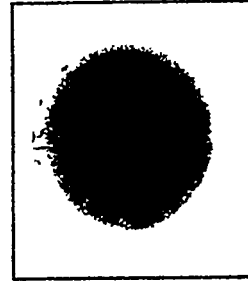
3 hrs @ 80°C



initial



initial



**IFO (8392) / B**

**IFO (8392) / A**

DET NORSKE VERITAS



DNV

### IFO / MDO Blends

#### MDO

#### IFO (8392)

VIS, cSt @ 50°C	347	<u>A</u>	-	<u>B</u>
cSt @ 40°C	-	3.9	3.2	899
DENS	991.7	856	899	855
TSP	0.06	nil	nil	855
CCAI	854	806		
BMCI / TE	76 / 60			

#### Blended Fuel Sediment (TSP), %

IFO / A	<u>TSE</u>	<u>TSP</u>
	U/F	3.0
IFO / B	0.02	0.03

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6th International Conference/Vancouver



## **SUMMARY / CONCLUSIONS**

### **How to Minimize Risk of Incompatibility**

- **Residual fuels with TE > 33 are “sensitive” fuels.**
  - » require careful selection of diluent
  - » best diluent is highest CCAI / lowest CI
- **Order of mixing is important**
  - » Add low BMCI component to high BMCI (high TE) component
- **Risk of incompatibility when mixing stable IFO’s is very low.**

## REFERENCES

- (1) Hulse, S.H., Thwaites, H. L., *Determining The Sediment Content of Fuel Oil - A New Method: I & EC (Analytical Edition):* Vol. 10 , No. 12, Dec. 1938.
- (2) Griffith, M. G., Siegmund, C. W., *Controlling Compatibility of Residual Fuel Oils:* ASTM Symposium on Marine Fuels, Miami, 7 - 8 Dec. 1983.
- (3) Martin, C. W. G., Bailey, D. R., *The Stability and Compatibility of Fuel Oil and Diesel Fuel:* J. Institute of Petroleum., Vol. 40, 1954, p. 138.
- (4) Van Kerkvoort, W. J., Nieuwstad, A. J. J., *Determination of Dry Sludge Content of Fuel Oils: Development of the Shell Hot Filtration Test (SHFT):* J. Institute of Petroleum, Vol. 37, 1951,596.
- (5) Lewis, C. P. G., Quillet, R , Schreuder, T., *Residual Fuel Oil Stability, Cleanliness Test Improved;* Oil & Gas Journal, April 8<sup>th</sup>, 1985.
- (6) Lewis, C. P. G., Johnson, E. K., Berryman, T. J., *The Stability of Residual Fuels - Theory and Practice of the Shell Concept:* Presented at 16<sup>th</sup> CIMAC Conference, Oslo, June 1985.
- (7) Berryman, T. J., Lewis, C. P. G., *Cleanliness and Stability of Residual Fuels:* ASTM Symposium on Marine Fuels, Orlando, 10<sup>th</sup> to 11<sup>th</sup> December 1987.
- (8) Lewis, C. P. G., de Jong, F., *Effects of Storage on the Stability of Residual Fuel Oil:* Paper No. 39, 3<sup>rd</sup> International Conference on Stability and Handling of Liquid Fuels, London, 13<sup>th</sup> to 16<sup>th</sup> Sept. 1988.
- (9) Shell, *Know Your Fuels:* Series Jan., 1990.
- (10) Herthaus, J. J., *Measurement and Significance of Asphaltene Peptization:* J. Institute of Petroleum, Vol. 48, 1962, p. 45.
- (11) (a) Por, N., Brodsky, N., Diamant, R., *Residual Fuel Oil Stability and Compatibility Studies:* (b) Rovesli, W. C., Anderson, R. P., *Prediction of Storage Stability and Compatibility of Residual Fuel Oils:* 3<sup>rd</sup> International Conference on Stability and Handling of Liquid Fuels, 13 Sept. 1998.
- (12) Anderson R. P., Pearson, C. D., Niper, Personal Communications: (a) *Toluene Equivalence Procedure for Residual Fuels, Titration Method:* (for EPRI) Sept. 1989. (b) Anderson, R. P., Reynolds, J. W., Niper, *Stability and Compatibility of Residual Fuel Oils:* EPRI, Proj. 2527-1, Dec. 1988.
- (13) Holmes, J. W., Bullin, J. A., *Fuel Oil Compatibility Probed:* Hydroc. Process, Sept. 1983.





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**A COMPUTERIZED SYSTEM FOR PREDICTION OF COMPATIBILITY OF  
FUEL OILS**

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Two fuel oils, thermally stable per se, may form suspended solids when mixed. Consequently, the blend will cause operating problems such as excessive centrifuge loading, strainer plugging and tank sludge formation. Though it is possible to check in laboratory whether two fuels are compatible, there are difficulties in obtaining a sample of fuel oil designated for the tank. Presently, it is impossible to decide, based on the data supplied with the fuel, what can be blended with what. Hence, there is a necessity for a predictive tool.

The aim of the present study was to develop a computerized system for prediction of compatibility of fuel oils.

Blends have been prepared. Their properties and thermal stability have been checked in the laboratory. An artificial neural network called "Back Propagation" has been chosen for feasibility studies. The system has been trained by supervised learning method. The properties of 235 blends and their constituents have been incorporated by the network.

Additional 78 blends were used in order to check the system's ability to predict compatibility between the constituents of new blends. The network predicted correctly the stability of 39, out of 42, unstable blends.

It was found that fuel oil forming incompatible blend with one fuel, may produce thermally stable blends with other fuel oils.

5 new incompatible combinations of fuel oils have been discovered.

It was proved that computerized neuron networks can be used for prediction of compatibility of fuel oil blends.

**ACKNOWLEDGEMENT**

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## Introduction

Almost every batch of fuel oil getting to the end user is a blend .

Refiners blend residues to achieve the desired viscosity. At it's final destination the fuel is mixed with residual remaining there from the previous delivery.

Blending of fuels from different origins often results in operational problems associated with incompatibility.

In Israel the situation is even worse. Our Electric Corporation, for instance, is obliged by environmental authorities to use at power stations fuel that is low in asphaltene and sulfur content, and purchases residual fuel from all over the world in order to achieve environmental and economic goals. As a result, problems of filter blocking occur from time to time.

To prevent such occurrences we tried to develop a computerized system for predicting stability of blends. The system is based on artificial intelligence and tries to mimic the brain's learning process. But before discussing the pros and cons of the computerized system, we would like to present some interesting experimental results regarding the incompatibility of residual fuels.

## Experimental

507 fuel oil blends have been prepared. 144 were unstable. The thermal stability of a blend was measured by ASTM D 4740 test. In some cases, the sludge formed instantaneously. In others, a week or two of storage at 50 °C were needed.

Prior to mixing, seven tests were performed on each fuel: density, pour point, viscosity, asphaltene content, sulfur content, Xylene Number and stability by ASTM D 4740. Only stable fuels were used for blend preparation.

Fuel oil 1025 formed incompatible blends with every fuel oil whose properties are defined in Table 1. According to the currently prevailing theory, fuel oil is a colloidal solution. Fuels with Xylene Number higher than 62 will form unstable blends with fuel oils that are produced from parafinic crudes. Whether fuel oil is parafinic or not can be deduced from the low density and a high pour point. By the same criteria, fuel oil 1025 is not of a parafinic origin. In this case we have a new unstable combination, that can't be explained by the theory of solubility.

Inspection of two additional pairs of fuels that formed a compatible and an incompatible blend upon mixing with fuel oil 813, Table 2, illustrates, that by knowing only : density, pour point, viscosity and Xylene Number, one couldn't predict which blend will be thermally stable and which will block filters upon usage.

Lets look at another pair of fuel oils that produced even more intriguing results. Fuel oil 791 resembles very much fuel oil 792. Nevertheless, one formed a compatible blend with fuel oil 819 while the other was unstable - Table 3.

After examining 507 mixtures, we were able to arrange unstable blends into 6 categories -Table 4 .

Category A: Any fuel oil whose density is under 0.97 kg/l at 15 °C will form an unstable blend when mixed with another fuel whose Xylene Number equals to or is above 62

This is a well known combination and can, easily, be explained by the current theory on fuel oil composition.

Category B: Any fuel oil whose density is above 0.98 kg/l at 15 °C, sulfur content under 1% and asphaltene content under 5% will cause sediment formation in the blend when mixed with fuel that has Xylene Number above 62. A good example is residual fuel 1025 (table 1).

Category C: Any fuel oil that is characterized by accelerated sediment ( IP 375 ) above 0.2% /w, will form an unstable blend when mixed with fuel oil that has a Xylene Number equal to or above 62. This phenomena can be explained by the current solubility theory.

Category D: Two fuel oils whose densities are above 0.98 kg/l at 15 °C, sulfur content under 1% and asphaltene content under 5% will form an incompatible blend when mixed together.

Category E: Fuel oil that is characterized by accelerated sediment above 0.2%/m and a pour point equal to or above 24 °C will form an unstable blend when mixed with fuel oil whose pour point is above 24 °C . We did not examine this sediment; it may consist of wax.

Category F: In this category unstable blends are formed by mixing fuel oils whose densities are above 0.98 kg/l at 15 °C, sulfur content under 1% and asphaltene content under 5%, with residual fuels of parafinic origin.

We made an attempt - unsuccessful until now - to explain these phenomena by using the viscosity index as an additional yardstick.

When one looks at the variety of possibilities, it is obvious that a computerized system will make a better job than a human expert.

## **The Computerized System**

By using the data gathered in laboratory experiments, the Back Propagation neural network has been trained to predict the compatibility between the two fuel oils in the blend. Artificial neural networks are computer models inspired by the structure and behaviour of real neurons in the human brain. The Back Propagation algorithm is a three layer network that learns from training examples. To train the network we present the input layer with the properties of the residual fuels involved in blend formation and the output layer with the stability of the blend as obtained by ASTM D 4740 test during laboratory experiments.

The network goes to and fro changing weights of the layer connections until the difference between the actual and the desired result is minimized. The weights at the end of the process are memorized by the computer. Optimization of the weights occurs by presenting the network with maximum examples.

The final product is a friendly program that consists of two screens:

### **The Prediction Screen ( Fig 1)**

The first screen is a screen for prediction of compatibility.

The properties of fuel oils are typed in the appropriate windows.

Pointing at the button "blend" results in the appearance of the blend properties on the left side of the screen.

Pointing at the button "study" gives the predicted compatibility at "the result" window. The output includes a declaration "stable" or "not stable" and a rating of compatibility.

### **The Training Screen ( Fig 2 )**

The second screen is a training screen and provides the option for updating the data stored in the computer. The properties of new fuel oils are typed in the appropriate windows. The thermal stability of the blend as obtained in laboratory is recorded. Then, a push on the button "study" starts the training of the program. From our experience, 300 repetitions, to and fro, are sufficient in order to minimize the difference between the actual result and the prediction of the program.

### **Forecast capability**

In order to evaluate the prediction capability of the finished program, we prepared 42 unstable and 36 stable blends. Their compatibility was tested in laboratory and compared with the forecast of the program.

We can see the results for unstable blends in Fig 3.

The prediction of the neural network was much less than desired. The system was able to foresee correctly only 57.89% of the unstable blends.

Addition of a new function to the system ( Fig 1 ) minimized the erroneous prediction to only 7% ( Fig. 4 ).

This function uses the six categories we presented previously (Table 4 ): after typing the properties of the two residual fuels in the appropriate windows, one points to the button "category". If the examined pair of fuel oils matches one of the six unstable categories, than an output "not stable" will appear.

In the case of stable blends the prediction is 95% correct when the first version of our program is used. By pointing to the "category" button the prediction becomes less perfect by 14.4%. We call this a compelled forecast ( Fig. 5 ).

## **Conclusions**

1. Blending of two residual fuel oils may result in sludge formation. The sediment formation is not always immediate and may take sometimes a week or two.
2. New combinations of fuel oils, that form sludge upon blending, have been identified.
3. A computer program, that is able to predict compatibility between fuel oils, has been developed.
4. This program was able to predict correctly incompatibility between two fuel oils in 93% of the cases.
5. The program is capable of updating itself.

**Table No. 1: Properties of fuel oils that formed sediment with fuel oil 1025**

Sample No.	1025	736	707	716	725
<b>Properties</b>					
Density, 15°C, Kg/l	0.9871	0.9951	0.9862	0.9885	0.9878
Pour Point, °C	+9	+9	+6	+9	+9
Viscosity, 50 °C, CST	281.5	371.0	387.5	402.5	395.0
Asphaltene Content, % m	3.9	9.8	6.4	6.6	6.6
Sulfur Content, % m	0.87	2.73	0.59	0.58	0.67
Xylene Number	40	62	62	67	63
Accelerated Sediment, % m	0.051	0.046	0.37	0.022	0.1
Viscosity Index	59	104	84.8	94	98

**Table No. 2: Fuel oil 813 - A comparison between properties of compatible and incompatible blends**

Sample No.	Incompatible blend (5)		A compatible blend (1)	
	813	802	813	805
<b>Properties</b>				
Density, 15°C, Kg/l	0.9599	0.9549	0.9599	0.9803
Pour Point, °C	+24	+24	+24	+24
Viscosity, 50 °C, CST	449.5	407.1	449.5	350.5
Viscosity, 100 °C, CST	36.5	35.8	36.5	30.9
Asphaltene Content, % m	5.9	5.5	5.9	6.3
Sulfur Content, % m	0.98	0.82	0.98	0.99
Xylene Number	47	37	47	37
Accelerated Sediment, % m	0.28	0.013	0.28	0.028
Viscosity Index	58	67	58	56
Computer Forecast	3- unstable		3- unstable	

**Table No. 3: Fuel oil 819 - A comparison between properties of compatible and incompatible blends**

Sample No.	Incompatible blend (4)		A compatible blend (1)	
	819	791	819	792
Density, 15°C, Kg/l	0.9851	0.9855	0.9851	0.9875
Pour Point, °C	+6	-3	+6	-3
Viscosity, 50 °C, CST	336.9	123.6	336.9	235.8
Viscosity, 100 °C, CST	28.75	15.20	28.75	24.70
Asphaltene Content, % m	5.7	5	5.7	4.8
Sulfur Content, % m	0.95	0.97	0.95	0.92
Xylene Number	57	47	57	27
Accelerated Sediment, % m	0.086	0.046	0.086	0.056
Viscosity Index	45	48	45	65
Computer Forecast	3- unstable		3- unstable	

**Table No. 4: Unstable Blends Classification**

Category	Fuel Oil A	Fuel Oil B
A	Density, 15°C, Kg/ l <0.97	Xylene No. ≥62
B	Density, 15°C, Kg/ l >0.98 Sulfur, % m ≤1 Asphaltenes, %m, ≤5	Xylene No. ≥62
C	Accelerated Sediment, % m ≥0.2	Xylene No. ≥62
D	Density, 15°C, Kg/ l >0.98 Sulfur, % m ≤1 Asphaltenes, %m, ≤5	Density, 15°C, Kg/ l >0.98 Sulfur, % m ≤1 Asphaltenes, %m, ≤5
E	Accelerated Sediment, % m ≥0.2 Pour Point, °C ≥24	Pour Point, °C ≥24
F	Density, 15°C, Kg/ l >0.98 Sulfur, % m ≤1 Asphaltenes, %m, ≤5	Density, 15°C, Kg/ l <0.97

Fig 1: The Prediction Screen

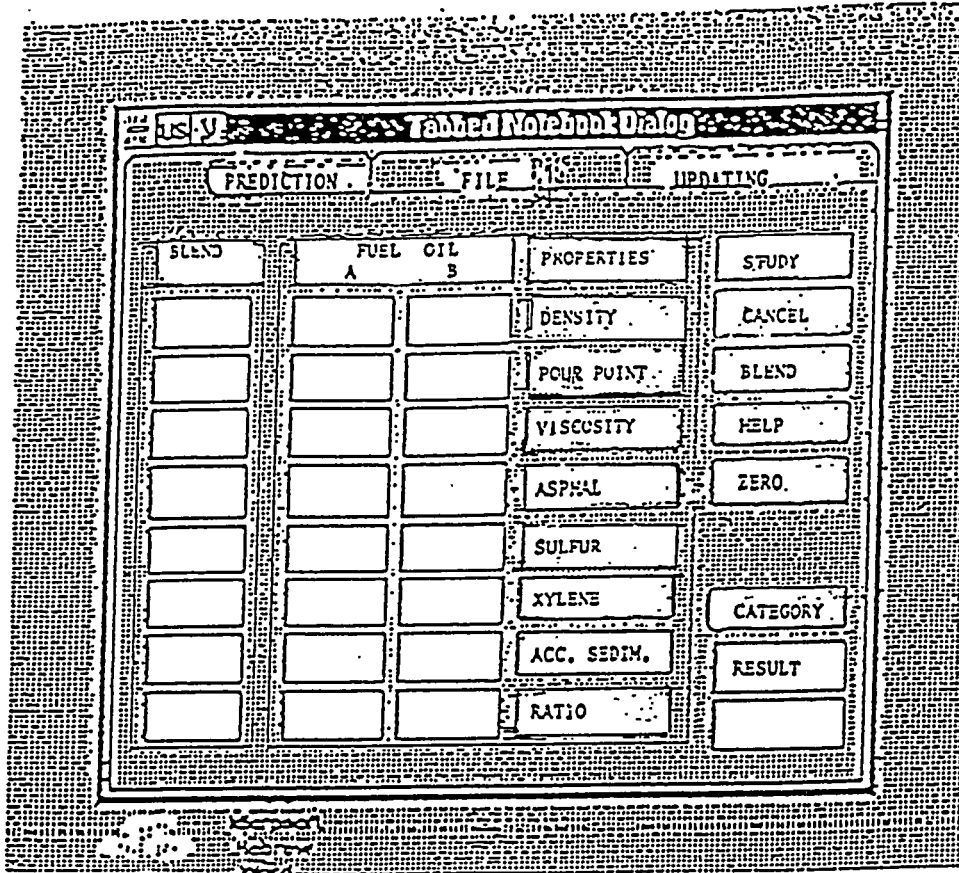


Fig 2: The Training Screen

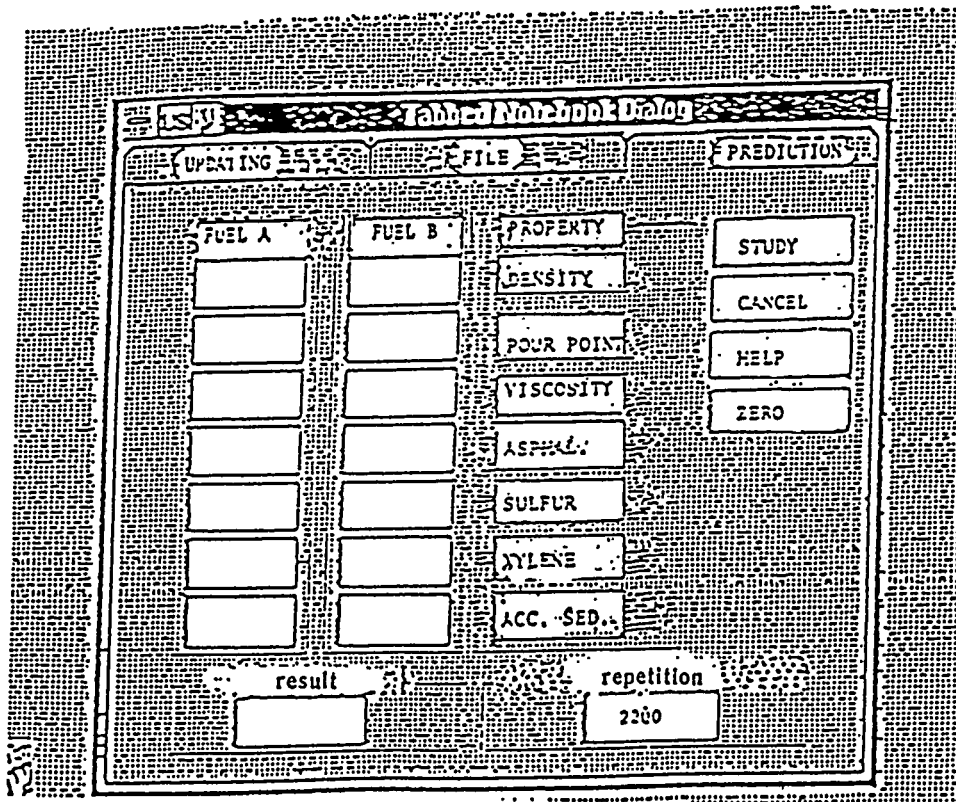




Fig. 3: The Prediction Capability of the Computerized System (before the Introduction of the Function "Category")

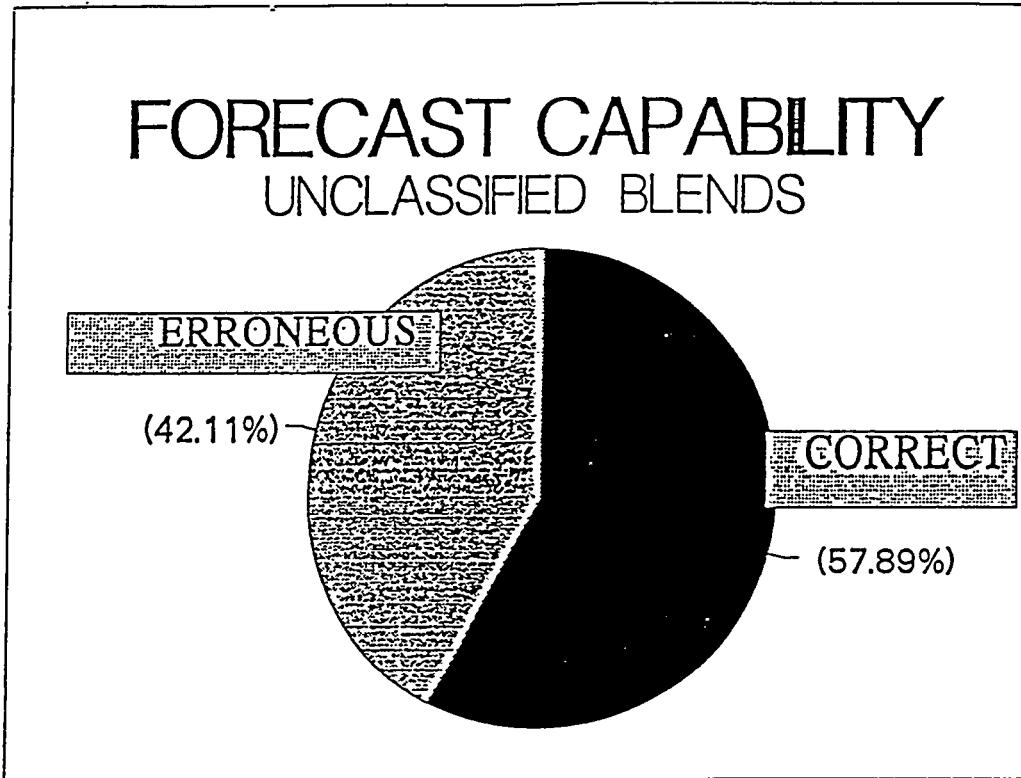
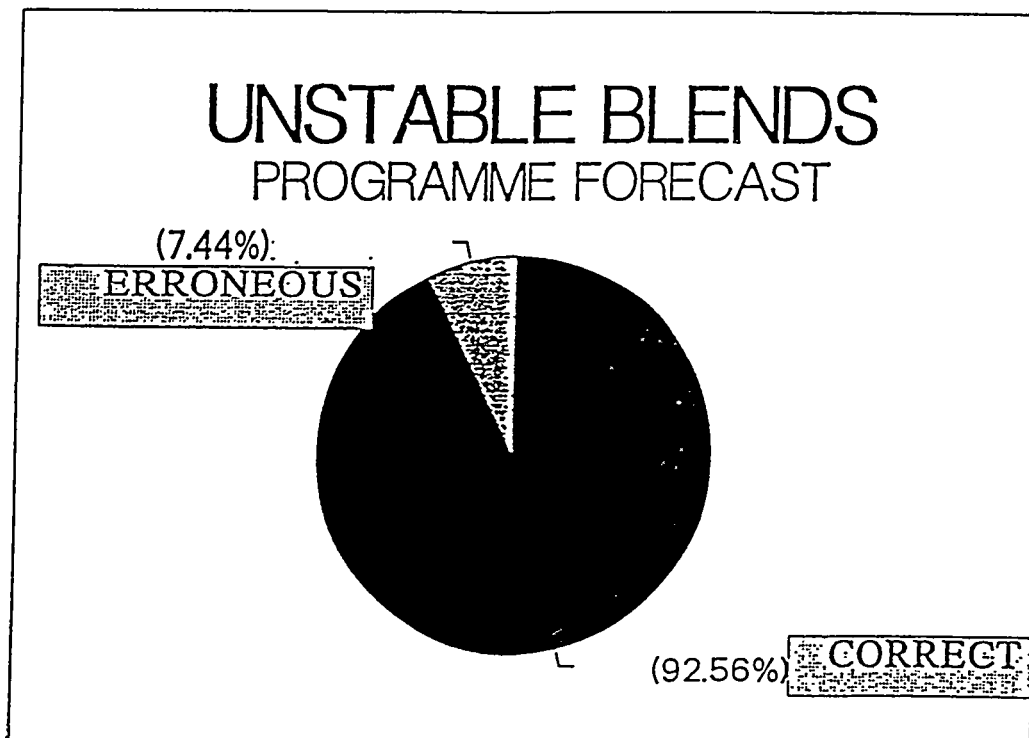
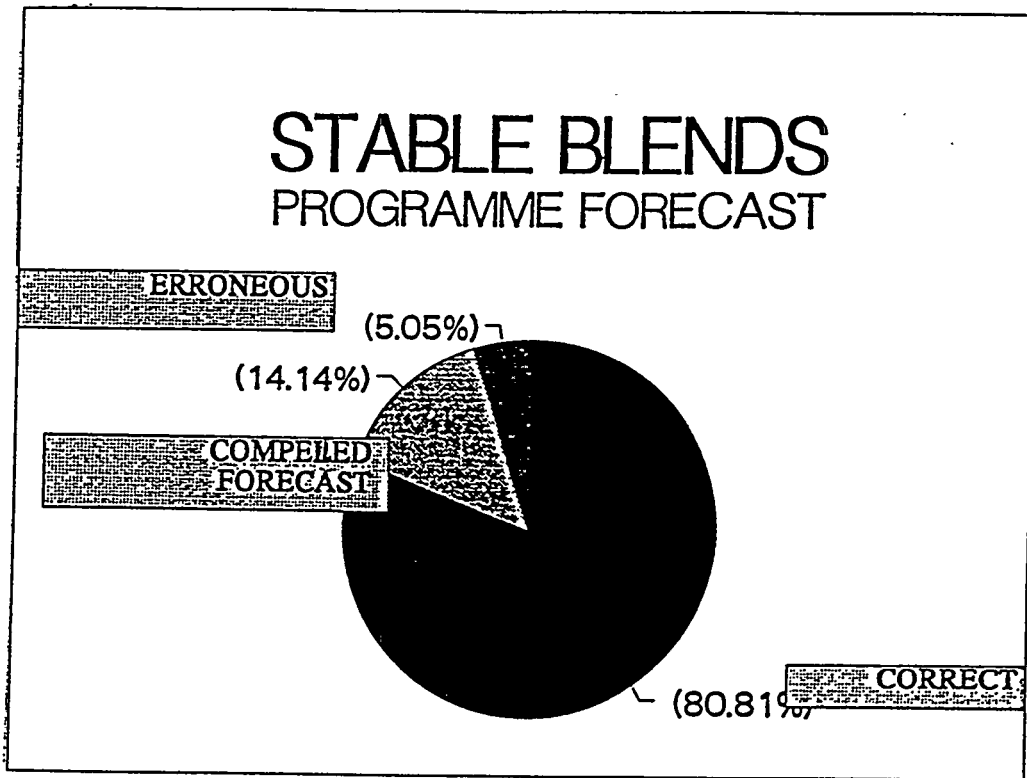


Fig. 4: The Prediction Capability of the Computerized System for Unstable Blends after Classification



**Fig. 5: The Prediction Capability of the Computerized System for Stable Blends**



*6th International Conference  
on Stability and Handling of Liquid Fuels*  
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**AN IMPROVED FUEL FILTERABILITY TEST**

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**Abstract**

This paper describes our efforts to improve upon existing filterability test methods used in the laboratory and in various field applications. Our goal has been to better define scaling parameters especially in regard to large scale fuel handling systems such as airport and shipboard systems and to improve test method reality by investigating various types of filter media. By carefully controlling the effective cross sectional area we have minimized the effects of sample viscosity on pressure drop. When sample viscosity is thus taken into account and all the other physical variables such as flow rate, pressure and temperature are also controlled then it is possible to use pressure drop to very accurately predict solid contamination concentration in fuel samples. This paper describes the rationale behind our selection of the controlled variables and presents the data which support these changes. Thus, these improvements should now allow us to use this type of filterability test which realistically mimics actual fuel systems and their associated filtration devices as much more accurate predictors of potential field problems.

**Introduction**

Since the beginning of middle distillate fuel use in turbine engine applications, filterability has been an important fuel property. Since this fuel property is often hard to measure quickly and accurately by the current ASTM methods, it would be desirable to be able to adopt a useful and realistic filtration method.

A realistic filterability test must incorporate standard filtration industry concerns such as liquid viscosities, filter media porosities, filter media pore size and scaling effects. Once this is done, it should be possible to correlate such a filterability test with real world filtration equipment. This kind of test should then prove useful to determine fuel cleanliness with both marine diesel fuel and aviation fuel as a field test and for laboratory quality assurance testing.

Previous work at the Naval Research Laboratory (NRL)<sup>1</sup> showed that the selection of a filter medium to simulate the real world filters must take into account the influence of both filter porosity and filter pore size. Figure 1 shows the filtering time vs the volume of tetradecane filtered, using gravity flow through three membrane filters of various pore sizes and equivalent porosities and through the presently used GF/A glass fiber filter with a nominal pore size of 1.5  $\mu\text{m}$ . Figure 2 shows the filtering time of tetradecane through the filtering material from three commercial filters. If the filtering times shown in these two figures are compared, it can be seen that in order to use a membrane filter in a laboratory test it must have a pore size between 3  $\mu\text{m}$  and 15  $\mu\text{m}$ .

In this work we apply these earlier results to select a filter medium and carefully control the flow rate and effective filtering area to develop a reliable, useful filterability test.

### Experimental

The apparatus (Figure 3) used to measure filterability is commercially available from EMCEE Electronics, Inc. It consists of an eight roller peristaltic pump capable of delivering 20 mL/min through 3 mm i.d., 6.1 mm o.d. tygon tubing with an initial delta pressure of 0 psi. A flow timer is set to deliver a maximum of 300 mL through the filter or up to a delta pressure reading of 25psi. A pressure transducer is used to measure the delta pressure through the filter and is displayed on a liquid crystal readout. Two additional liquid crystal readouts show the milliliters filtered to obtain the displayed pressure. The first of these two readouts shows the number of milliliters filtered to obtain a pressure of 0 to 15 psi and the second readout shows the number of milliliters filtered to obtain a pressure of 0 to 25 psi or the maximum of 300 mL. The filters used were 5.0  $\mu\text{m}$  nylon membranes from Micron Separations, Inc., Westboro, MA, Catalog Number R50SP02500, placed in a filter holder so that the effective filtering area was 1.77  $\text{cm}^2$ .

The test fuels used were two current production diesel fuels with viscosities of 4.2 cSt and 3.8 cSt at 20°C. The natural sediment used was the filterable contamination from diesel fuels that had

been stored at ambient temperatures. This sediment was collected on nylon membrane filters with a pore size of 0.8  $\mu\text{m}$ , rinsed with heptane and dried at 100°C and then removed from the filter. A scanning electron microscope was used to determine the particle size distribution of this dry sediment.

The 5  $\mu\text{m}$  and 3  $\mu\text{m}$  monodispersed silica gel used as test contaminants were obtained from Whatman, Inc. Monodispersed latex beads of 1  $\mu\text{m}$ , 3  $\mu\text{m}$  and 6  $\mu\text{m}$  were obtained from Polysciences, Inc. The latex bead sizes were determined in water using a Brookhaven Particle Sizer operating on the principle of centrifugal photosedimentation.

## **Results and Discussion**

In order to establish the test conditions and criteria necessary to have a viable filterability test, a series of experiments were carried out using varying amounts of solid particles of known sizes as dopants in a current production diesel fuel with a viscosity of either 4.2 cSt or 3.8 cSt at 20°C.

The first tests were done using a natural sediment or sludge which was filtered from a diesel fuel that had been aged at room temperature. The sediment was dried and then removed from the filter. This sediment was then accurately weighed into a diesel fuel at levels of 5, 10 and 15 mg/L. To insure that the sediment would remain suspended throughout the fuel for the duration of the filterability test, it was stirred vigorously with a stirring rod and then sonicated for 5 minutes and then run immediately. Figure 4 shows that there was a very good linear relationship between the amount of sediment in the fuel and the pressure across the filter. Although this work proved to be successful it was terminated because of the lack of the natural sediment.

The next tests were done with a 3 $\mu\text{m}$  and a 5 $\mu\text{m}$  monodispersed silica gel. Varying amounts, from 10 to 100 mg/L, of the 5  $\mu\text{m}$  silica gel were carefully weighed into a diesel fuel. The sample was stirred vigorously and sonicated for 5 minutes and then run immediately on the filterability apparatus. Figure 5 shows that over this range of contamination there was a good linear relationship with the delta pressure. Amounts of the 3  $\mu\text{m}$  silica gel, from 10 to 70 mg/L, were

next added to the diesel fuel and tested under the same conditions. There was a good linear relationship over this range of contamination but added amounts over 70 mg/L caused a pressure buildup of greater than 25 psi before the full 300 mLs were filtered.

Polystyrene latex beads of 1 $\mu$ m, 3 $\mu$ m and 6  $\mu$ m diameter were next tried as contaminants. The 1  $\mu$ m beads at a level of 10 mg/L caused a pressure buildup of greater than 25 psi before the full 300 mL of fuel was filtered and the 3  $\mu$ m diameter beads at the same 10 mg/L level gave a pressure of 21 psi when 300 mL was filtered so use of those two sizes was not continued . The 6  $\mu$ m diameter latex beads were added to a diesel fuel at levels of 10, 20 and 30 mgs/L and tested under the same conditions also showed a good linear relationship (Figure 6).

Table 1 compares the pressures obtained using the filterability instrument for various diameter particles added to a diesel fuel at a 10 mg/L level. It has been widely accepted that natural sediment is approximately 1  $\mu$ m in diameter but this measurement has always been made on dry sediment using a Scanning Electron Microscope. Comparing the pressure of 12 psi obtained with the natural sediment and the pressures obtained for the three sizes of latex beads, which have been sized in water using a Brookhaven Particle Sizer it can be seen that the natural sediment in fuel is probably closer to 5  $\mu$ m in diameter when in a fuel.

Twenty commercial marine diesel fuels from the 1996 Navy World Wide Survey were used to examine the relationship between amount of existing sediment in each sample determined gravimetrically and the delta pressure measured on the filterability apparatus. Figure 7 shows that although there were a few samples that showed some agreement, there was little overall correlation when actual diesel fuel samples were tested. A contamination level of 10 mgs/L or more can cause filterability and equipment problems.

### **Conclusions**

This study shows that the test conditions which were use, including filter pore size of 5  $\mu$ m,

effective filtering area of 1.77 sq. cm. and flow rate of 20 mL/min, are realistic and can be used in an improved filterability test. These conditions more accurately mimic actual fuel systems and their associated filtration devices.

Testing of real fuels showed that there was really no correlation between the weight of existing particulate contamination and the delta pressure given by the filterability test. There was a big fuel/type of sediment dependency. However, if a test method is developed using a delta pressure criterion only, this correlation is not necessary.

Pressures obtained using the filterability instrument for various test particles of controlled diameters in diesel fuel shows that the typical existing sediment (sludge) is closer to 5 um than to the 1 um as previously thought.

A method using this filterability instrument could be used in fuel specifications as a replacement for the present method using filter blocking measurements and all methods using gravimetry to determine particulate contamination of diesel fuel and could prove useful in testing aviation fuel cleanliness. The instrument could be used as a compact, portable shipboard or field test kit. It is possible that this test could be used to predict filter/coalescer life.

### **Acknowledgment**

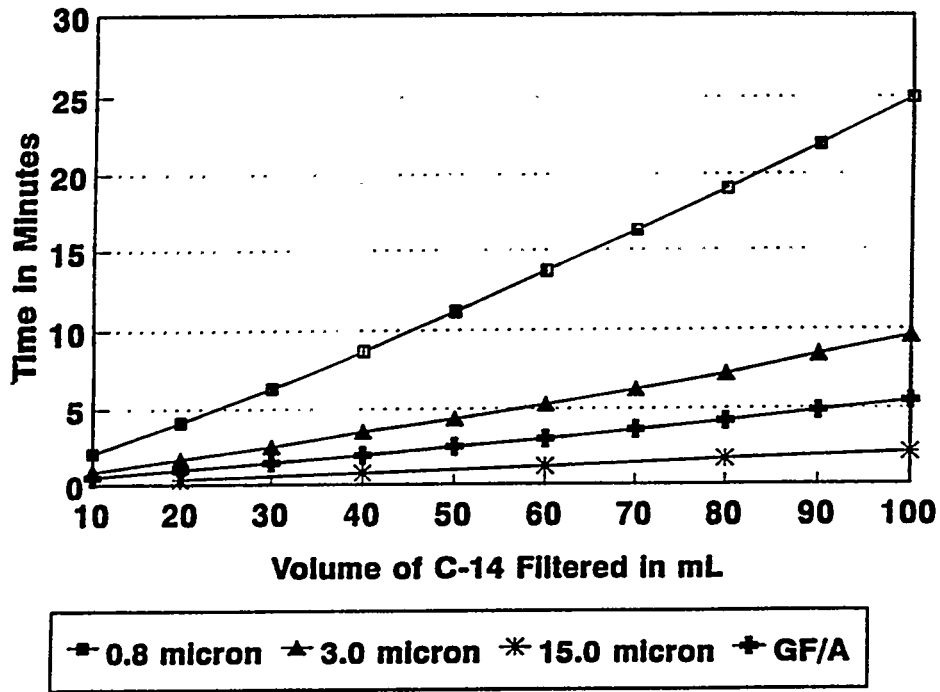
This study was partially funded by the Office of Naval Research.

## Reference

1. Hardy, D. R.; Beal, E. J. and Hughes, J. M., *Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels*, Giles, H. N., (Ed); U. S. Department of Energy, Washington, D. C., 1995, 449-461.

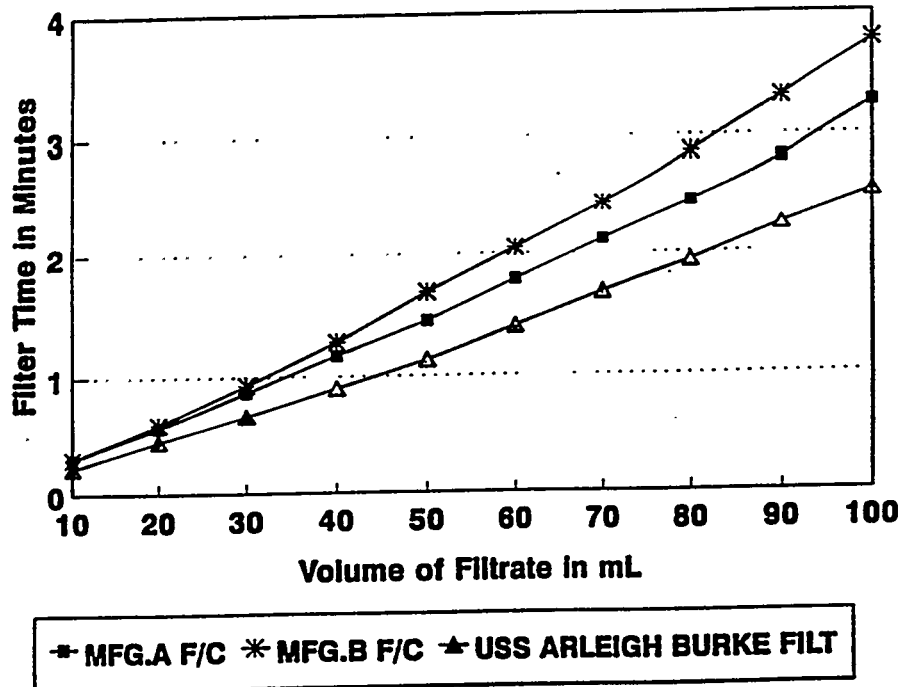


## Effect of Pore Size on Filtration Time "Equivalent" Porosity Membrane Filters

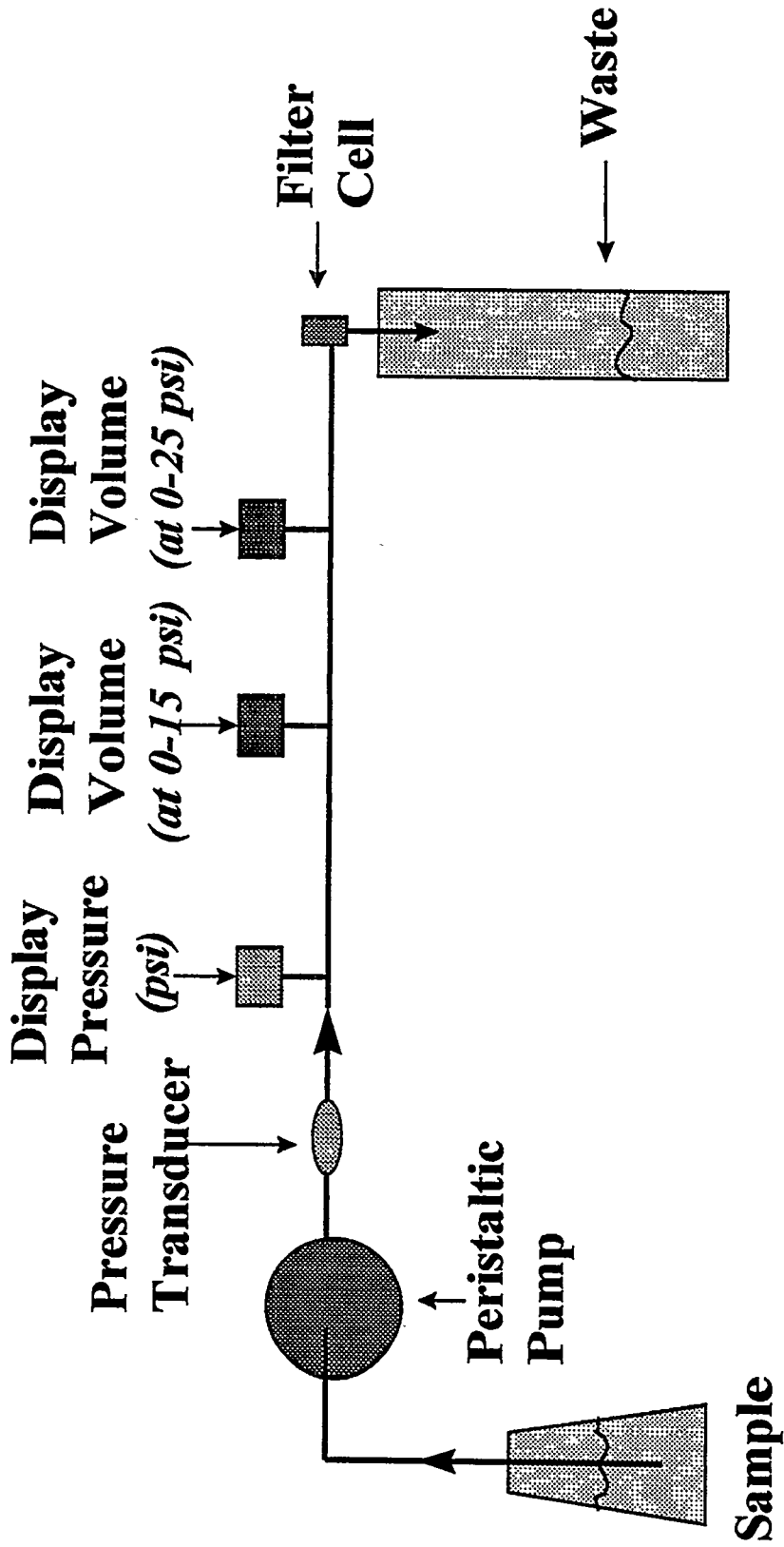


**Figure 1.**

## Porosity of 3 Commercial Filters



**Figure 2.**



**Figure 3. Schematic Diagram of Filterability Apparatus**

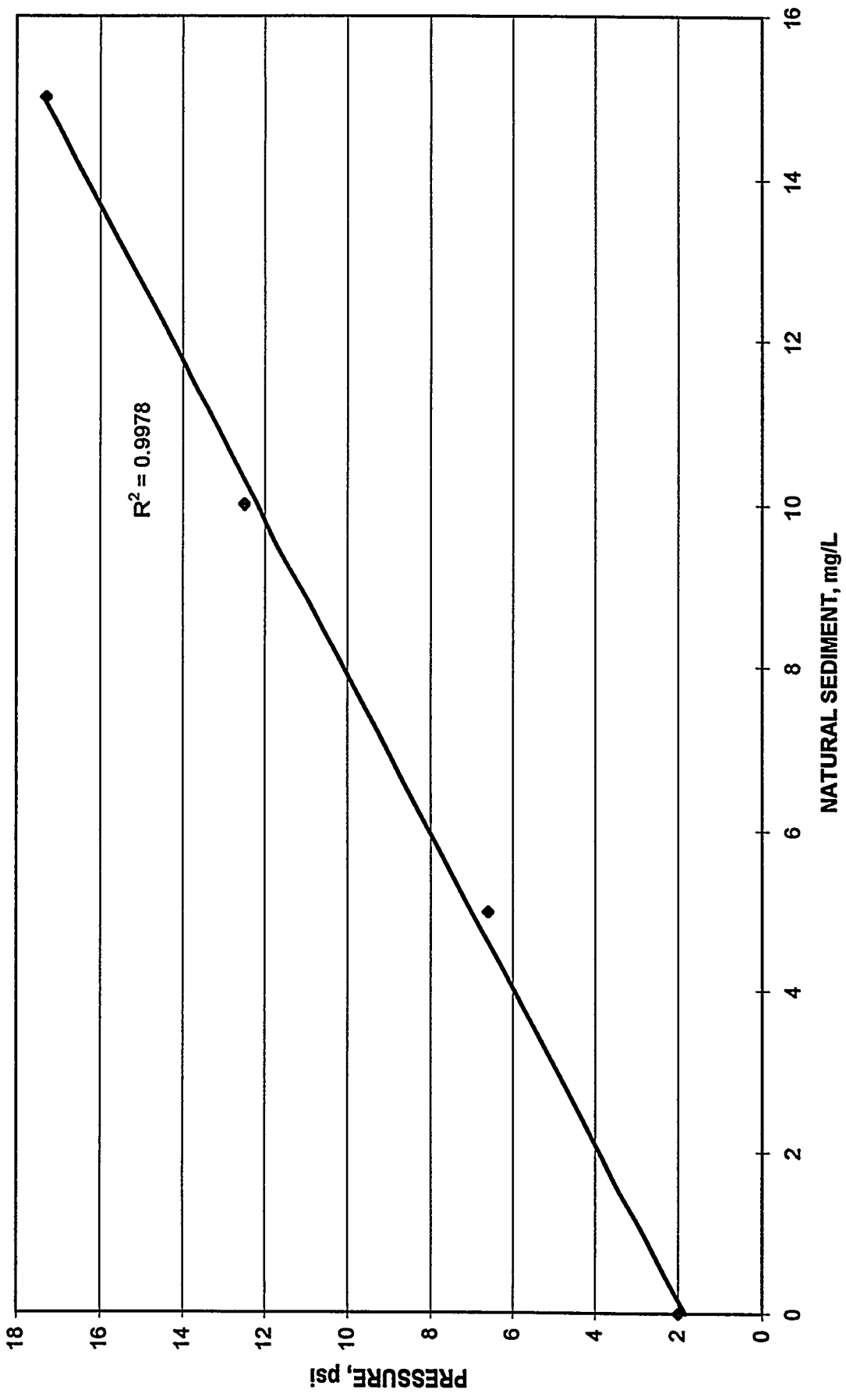


FIGURE 4. DELTA PRESSURE VS VARYING CONCENTRATIONS OF NATURAL SEDIMENT

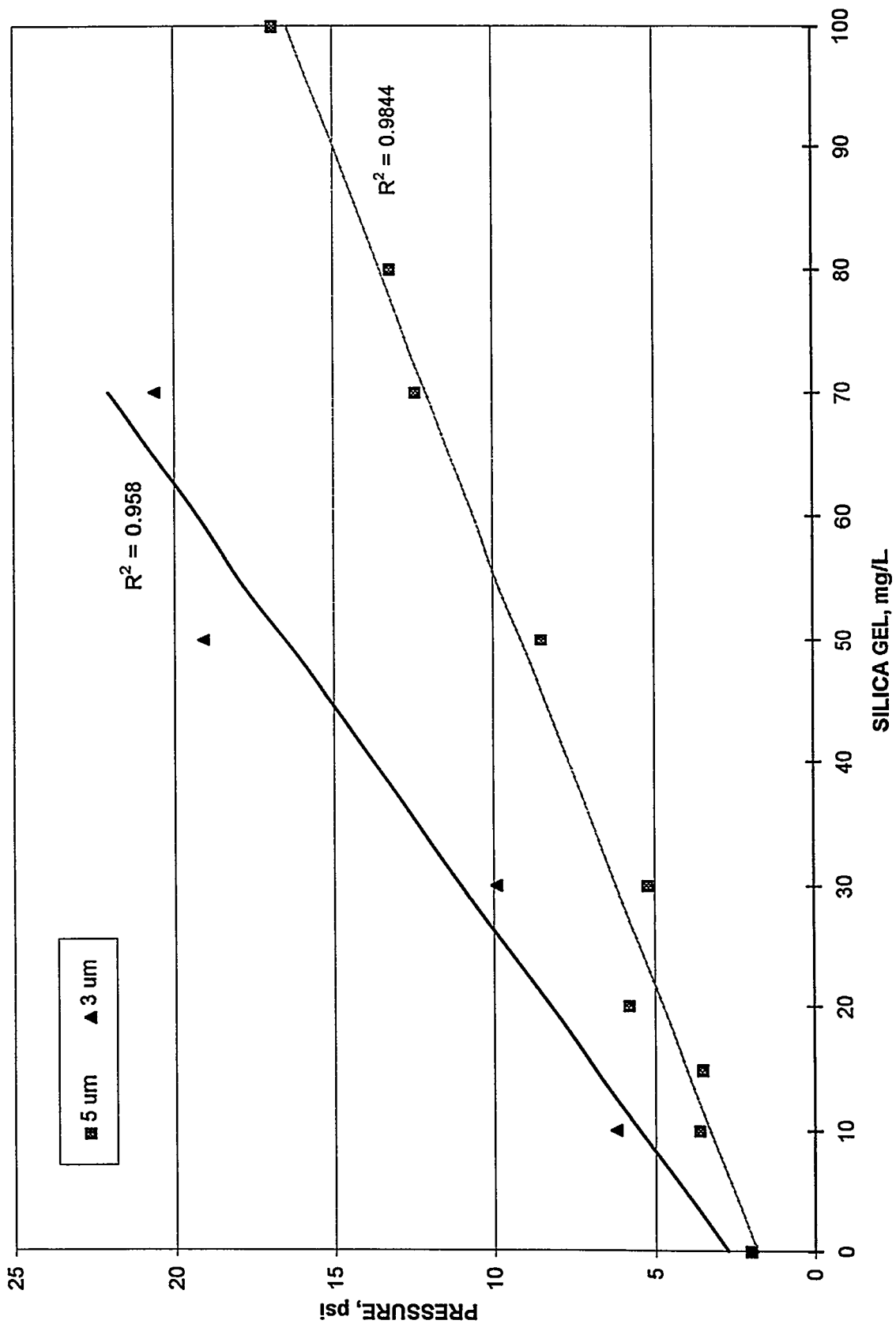


FIGURE 5. DELTA PRESSURE VS VARYING CONCENTRATIONS OF SILICA GEL IN DIESEL FUEL

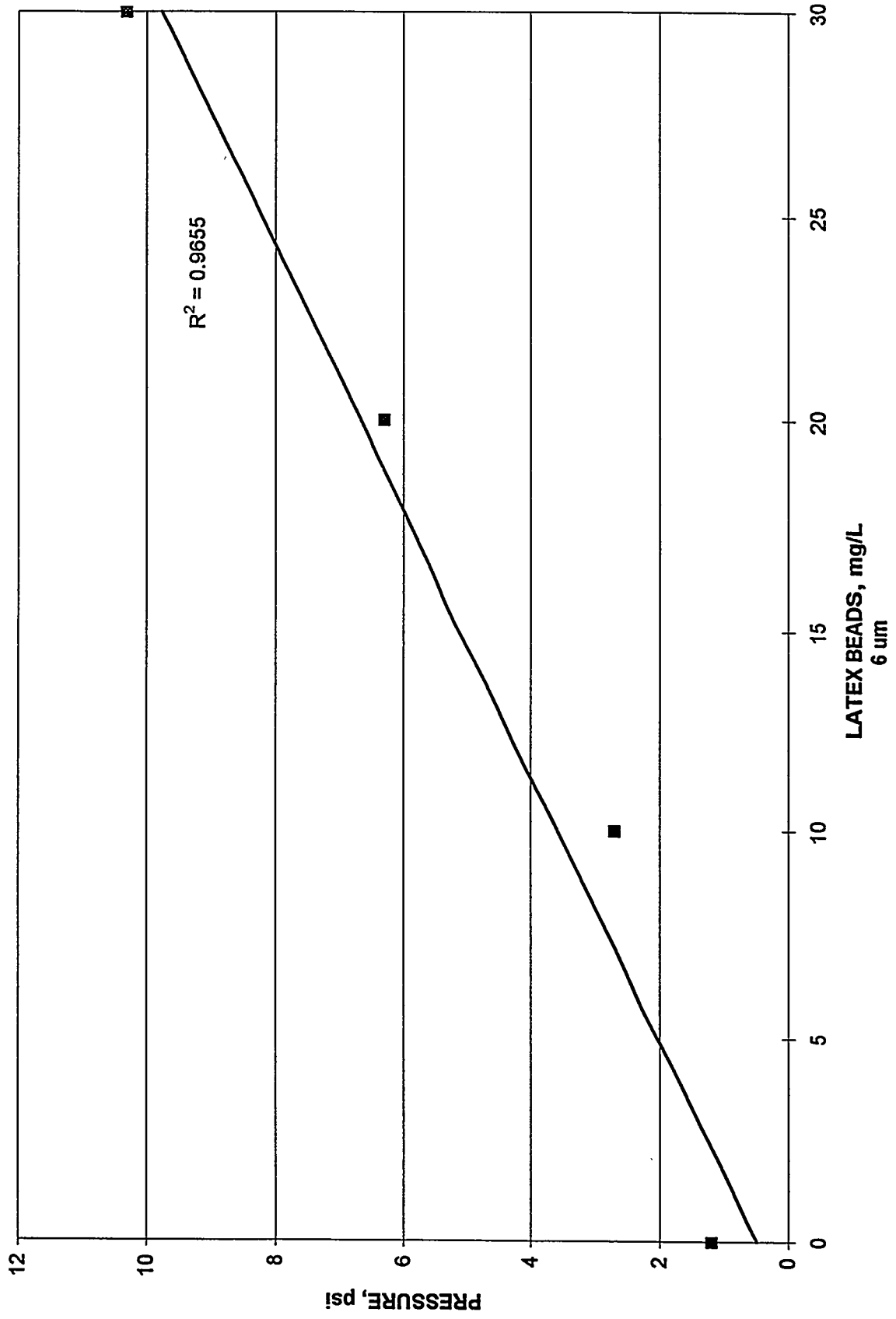
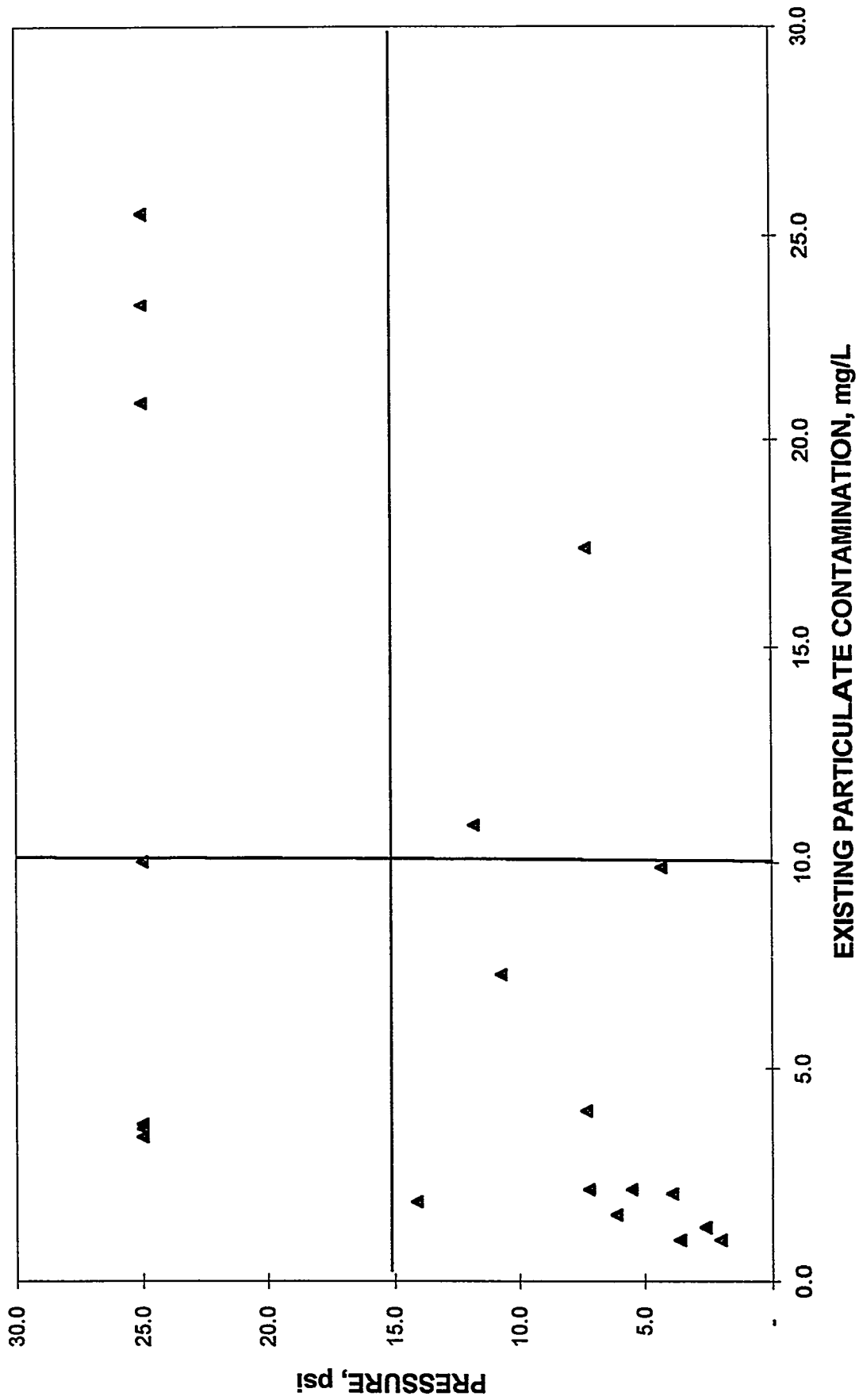


FIGURE 6. DELTA PRESSURE VS VARYING CONCENTRATIONS OF LATEX BEADS



**FIGURE 7. DELTA PRESSURE VS EXISTING PARTICULATE CONTAMINATION BY GRAVIMETRY**

**Table 1. Delta Pressure and Particle Size  
(10 mg/L of Particles Added to Fuel)**

Material	Pressure (psi)	Diameter ( $\mu\text{m}$ )	Method
natural sediment	12	~1	dry SEM*
latex beads	>>25	1	BPS**
latex beads	21	3	BPS**
latex beads	3	6	BPS**

\*Scanning electron microscopy of the dry sediment

\*\*Brookhaven Particle Sizer - centrifugal photosedimentation





*6th International Conference  
on Stability and Handling of Liquid Fuels*

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**RAPID DETAILED CHEMICAL ANALYSIS OF TRANSPORTATION FUELS BY  
GC-FIMS**

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**ABSTRACT**

Determination of the detailed molecular composition of transportation fuels by standard GC and GC-MS techniques is limited to gasolines only. The complexity of higher boiling fuels makes it extremely difficult to obtain reliable composition data by using these methods. Unlike many other ionization techniques, field ionization produces only the molecular ions for most compounds, and thus simplifies the analysis. However, because compounds of different classes sometimes share the same nominal mass, it is not possible to get detailed compound type analysis by FIMS alone. We have modified an HP 5971A Mass Selective Detector by replacing its standard electron-impact source with a volcano-style field ionization source developed at SRI. Several samples, including gasolines, jet, and diesel fuels as well as Arabian sweet crude oil were analyzed by this GC-FIMS. The chromatography was not optimized, with typical run times being on the order of 12 min. The total ion current chromatogram showed the expected poorly resolved hump. However, examination of selected ion chromatograms clearly showed well-separated peaks for different compound types sharing the same nominal mass. This information was used to prepare tables giving the detailed composition of the fuel. These results clearly show the feasibility of using GC-FIMS for rapid and quantitative analysis of transportation fuels.

**INTRODUCTION**

Field Ionization Mass Spectrometry (FIMS) has proven to be an invaluable technique for the analysis of complex mixtures, particularly fossil fuels. For most compounds, field ionization produces only the molecular ions. However, molecular weight alone is not sufficient to uniquely identify the class of a given hydrocarbon. For example, nonane—an acyclic saturate, and naphthalene—a diaromatic, both share the same nominal mass of 128. Such cases can be resolved by either high resolution mass spectrometry, or some chromatographic separation. Detailed analysis of fossil fuels up through heavy gas oils by FIMS has been well established at SRI through support of numerous agencies, including the Naval Research Laboratory on the analysis of middle distillates by high-resolution FIMS<sup>1</sup> and on the chemistry of storage stability of diesel fuels.<sup>2</sup> With that previous background, we felt certain that a GC-MS instrument retrofitted with an

FI source could be used for the rapid and quantitative characterization of a wide range of refined fuels, including gasoline, diesel, and aviation fuel.

An extensive background of the existing analysis methods for fuels will not be provided here, except to note that using current technology only the analysis of "simple" fuels such as gasoline is possible with a GC-MS system such as the mass selective detector (MSD) by Hewlett Packard (HP). Even for these fuels, special equipment is needed (multi-column automated GC), analysis time is long (up to several hours), extensive sample preparation may be required (multiple separations), and laborious data manipulation is needed.<sup>3</sup> The analysis of more complex mixtures (such as diesel and jet fuels) is not even attempted using these systems as the number of components is too large, and the overlap of the peaks too severe to allow any meaningful analysis. This remains the case as long as the entire burden of resolution is placed on the gas chromatograph. GC-MS techniques could work, however the commonly employed electron-impact method for making ions results in extensive fragmentation which limits the use of the mass spectrometer to only confirm the nature of a compound, but not to resolve mixtures of co-eluting components. Wadsworth and Vilalanti have demonstrated that by using NO as the chemical-ionization reagent gas they can get pseudo molecular ions ( $M+1$ ,  $M$ , or  $M-1$ ) for the hydrocarbons in fuels, and they have reported on a GC-MS system using this technique.<sup>4</sup>

GC and FIMS complement each other in their ability to separate compounds. For example, if we consider a pair of compounds likely to be found in transportation fuels such as n-nonane and naphthalene, FIMS alone could separate them, but only if one uses a high resolution mass analyzer because the exact masses of their molecular ions differ by only about 90 mDa. On the other hand, these compounds have widely differing boiling points (151°C for n-nonane and 218°C for naphthalene), and GC would have no problems in separating them. Now, if we consider another pair of compounds, n-nonane and propylcyclohexane, the situation is reversed. These compounds have molecular masses differing by 2.0 Da, and even a simple quadrupole mass spectrometer would have no difficulty separating them. However, because their boiling points are relatively close (151 vs. 157°C), a GC would have a more difficult time resolving them. By sharing the burden of resolution between GC and FIMS, the difficulties associated with either situation are easily overcome, and the complex task of obtaining detailed chemical analysis of even jet and diesel fuels is achievable.

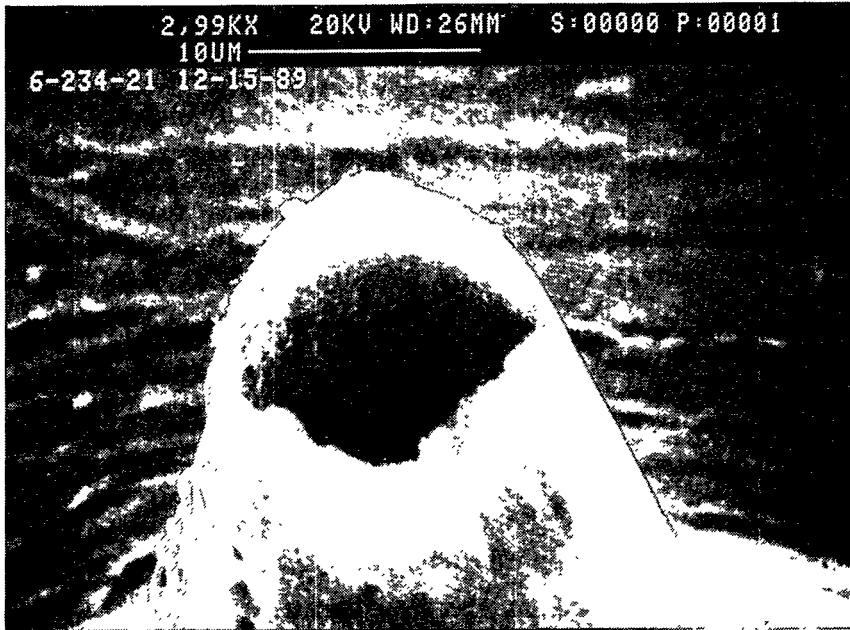
## INSTRUMENT MODIFICATION

The use of a mass spectrometer as a detector for a gas chromatograph is a well-established technology that has been developed into a high degree of sophistication and simplicity as demonstrated by the Finnigan MAT ion trap detector (ITD) and the HP MSD. Both the ITD and the MSD are designed to be turn-key instruments requiring minimal interaction with the user other than through the computer interface for operation. Thus, in putting together a GC-FIMS instrument, one of our objectives was to minimize the modifications to a commercial instrument in order to retain as many of its user-friendly features as possible.

We have replaced the electron-impact ionizer of an HP GC-MS system with an SRI volcano-style field ionizer.<sup>5</sup> Figure 1 shows a scanning electron micrograph of this microfabricated source. The molecules of interest are constrained to pass through the throat of the volcano and into a region of high field strength. The requisite field strengths are produced by the submicroscopic carbon dendrites along the rim of the volcano clearly visible in the lower portion of the Figure. When a modest potential of 1.0 to 1.5 kV is applied between the volcano and a closely spaced counter electrode (not shown in Figure 1), abundant field ionization is observed. We designed the field ionizer source to fit exactly in the space for the electron-impact ionizer of the MSD (Figure 2) to facilitate easy switching between the two modes of ionization.

The only substantive modification required to use a volcano FI source with the MSD involves a change in the interface between the GC column and the ionizer. The primary difference is that the *entire column* flow is directed through the volcano source, thus maximizing the ionization signal by using all of the eluting material. This arrangement is possible with the volcano-style FI source for two reasons. First, the FI source does not ionize helium and therefore the carrier gas is of no concern. Second, the very small gas conductance of the volcano ( $7.8 \times 10^{-4}$  liters/s for helium at 200°C through a 10- $\mu$ m diameter volcano), when combined with the carrier gas flow rate and MSD system pumping speed, results in an acceptable ion source operating pressure.

Operation of a volcano-style FI source with the MSD requires some changes in the analysis procedure. To begin with, tuning of the MSD is no longer possible using the omnipresent background of permanent gases—which are not ionized by the FI source, or by the standard fluorinated calibration compounds—which do not yield the necessary marker peaks during FI. We overcame this limitation by introducing a continuous stream of a three-component mixture consisting of acetone (58 Da), toluene (92 Da) and n-butylbenzene (134 Da). Within a short time



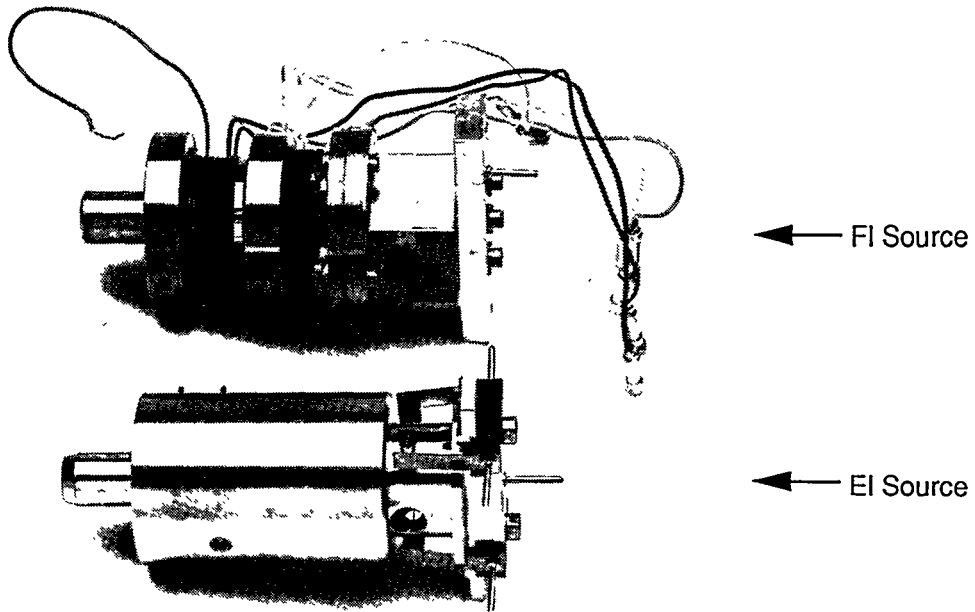
(a) Volcano before activation.



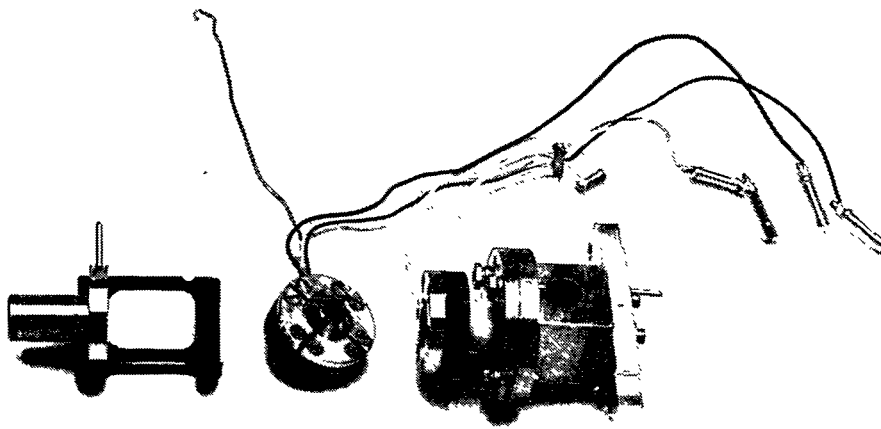
(b) Volcano after activation using a mixture of acetone, toluene, and butyl benzene.

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Figure 1. Scanning electron micrograph of the SRI volcano-style field ionization source.



(a) Comparison of standard EI source and modified FI source.



(b) Exploded view of FI source.

RP-8074-6

Figure 2. Photographs showing the standard EI-source and SRI's FI source for the MSD.

all three components simultaneously elute from the column, and the instrument can be conveniently tuned on the strong molecular ion signals.

We present here results of the analysis of several transportation fuels covering gasolines, aviation fuels, and diesels. We have used a 37-m  $\times$  0.2 mm SP2100 non-bonded column (HP5-MS), which separates components by boiling point. Initial tests were run by using a 23°C/min. linear heating rate starting at 70°C and heating the column up to 300°C. No optimization of the chromatography was attempted. Nevertheless, the results presented here demonstrate the feasibility of this approach. Subsequently, we have switched to a lower heating rate (17°C/min.) and a lower starting temperature (45°C) to capture the light ends better.

## RESULTS AND DISCUSSION

### Total Ion Chromatograms

The total ion chromatograms (TIC) for a gasoline, jet, and a diesel fuel are shown respectively in Figures 3. The elution of the gasoline sample is over in about 6 min. The TIC consists largely of reasonably well-resolved peaks. Thus, it is not surprising that with a little more optimization, gasoline samples can be analyzed by GC alone. The elution time for the jet fuel is 8 min. and that of the diesel is less than 11 min. These are relatively short elution times, and not unexpectedly, the TICs consist of a broad unresolved hump with a few spikes. However, as discussed below, we can get detailed chemical analysis from even these poorly resolved chromatograms when we examine the selected ion chromatograms.

The complexity of the chromatogram of a JP-5 jet fuel (NAPC 22) shown in Figure 3b is obvious and resolution of individual components would not be practical. Figure 4 shows the mass spectrum corresponding to the peak at 4.51 min. (marked with an asterisk). The FI-mass spectrum of the chromatographic peak is very clean and gives a strong signal for the parent compound at  $m/z$  128. A peak with this mass could result from either nonane or naphthalene. Examination of the ion chromatograms makes it clear the peak is due to naphthalene. Figure 5 shows the ion chromatograms for  $m/z$  128, 142, 156, 170, 184, and 198. These masses correspond to the homologous series of acyclic saturates and alkyl naphthalenes. The chromatogram for  $m/z$  128 shows a sharp peak at 4.5 min. corresponding to naphthalene. There is also a very weak peak at around 2.7 min. which would correspond to nonanes. The chromatogram for mass 142 shows two peaks at 4.80 and 4.94 min. due to the two isomers of methyl naphthalene, as well as a peak at 3.2 min. for decanes. At higher masses we can see the growing importance of the alkanes in the

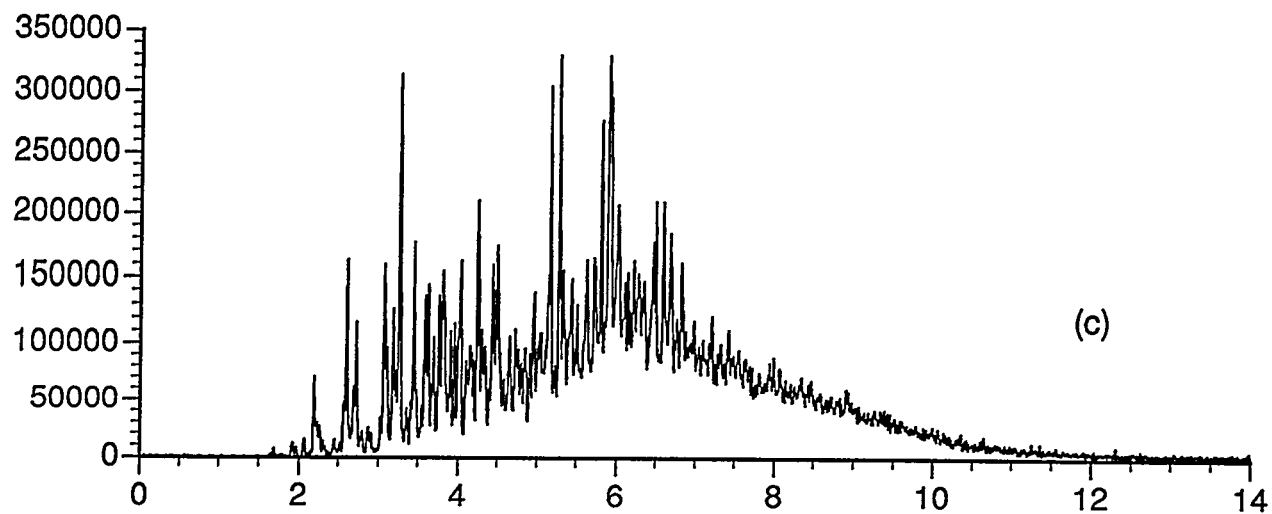
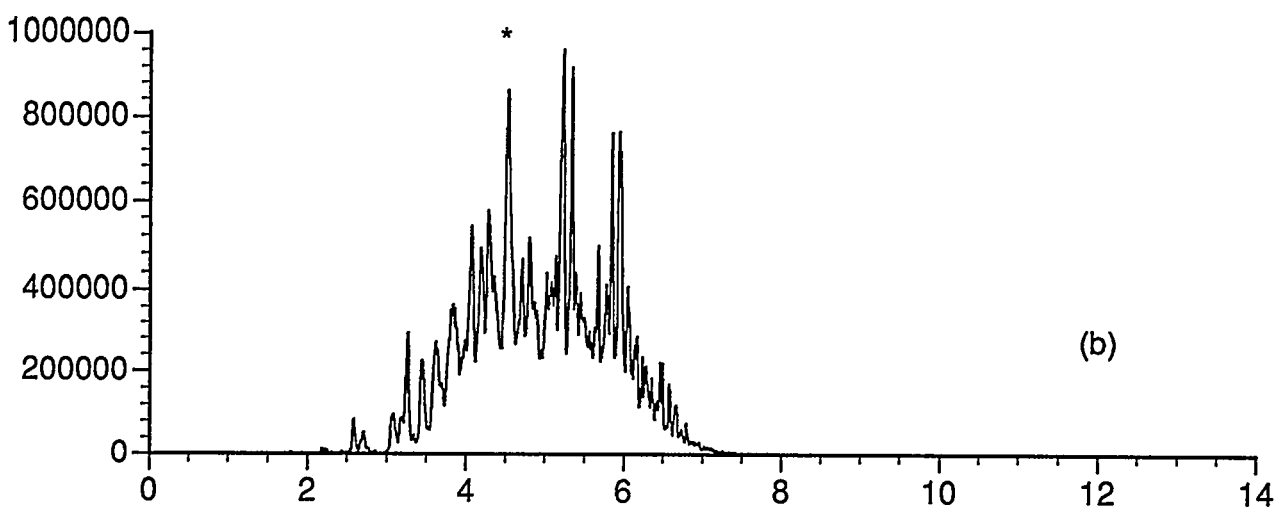
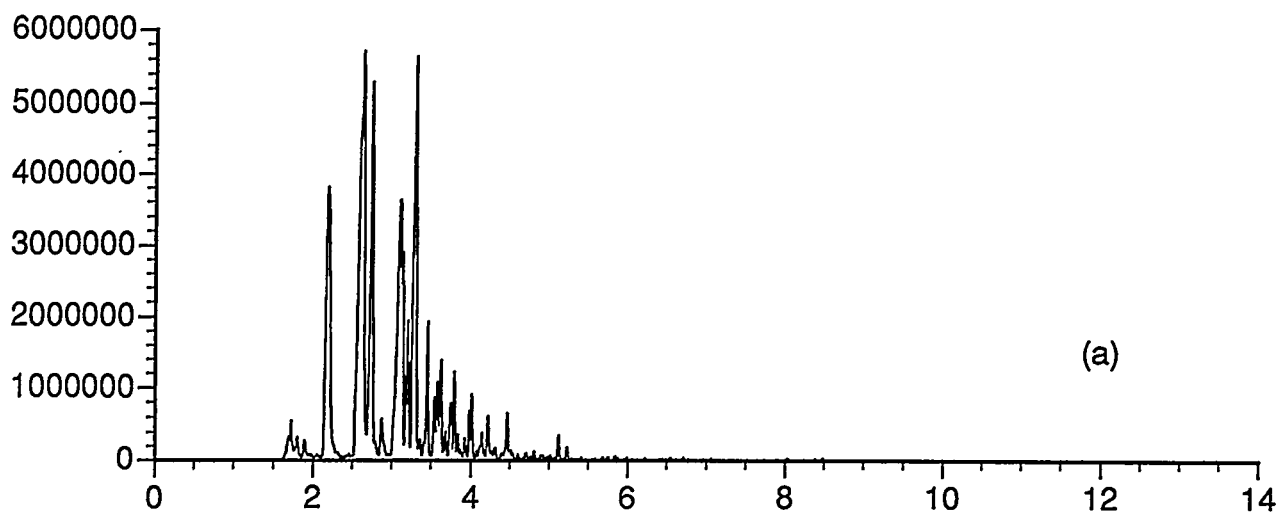


Figure 3. GC-FIMS total ion chromatograms for (a) an unleaded gasoline, (b) a JP-5 jet fuel, and (c) a diesel.

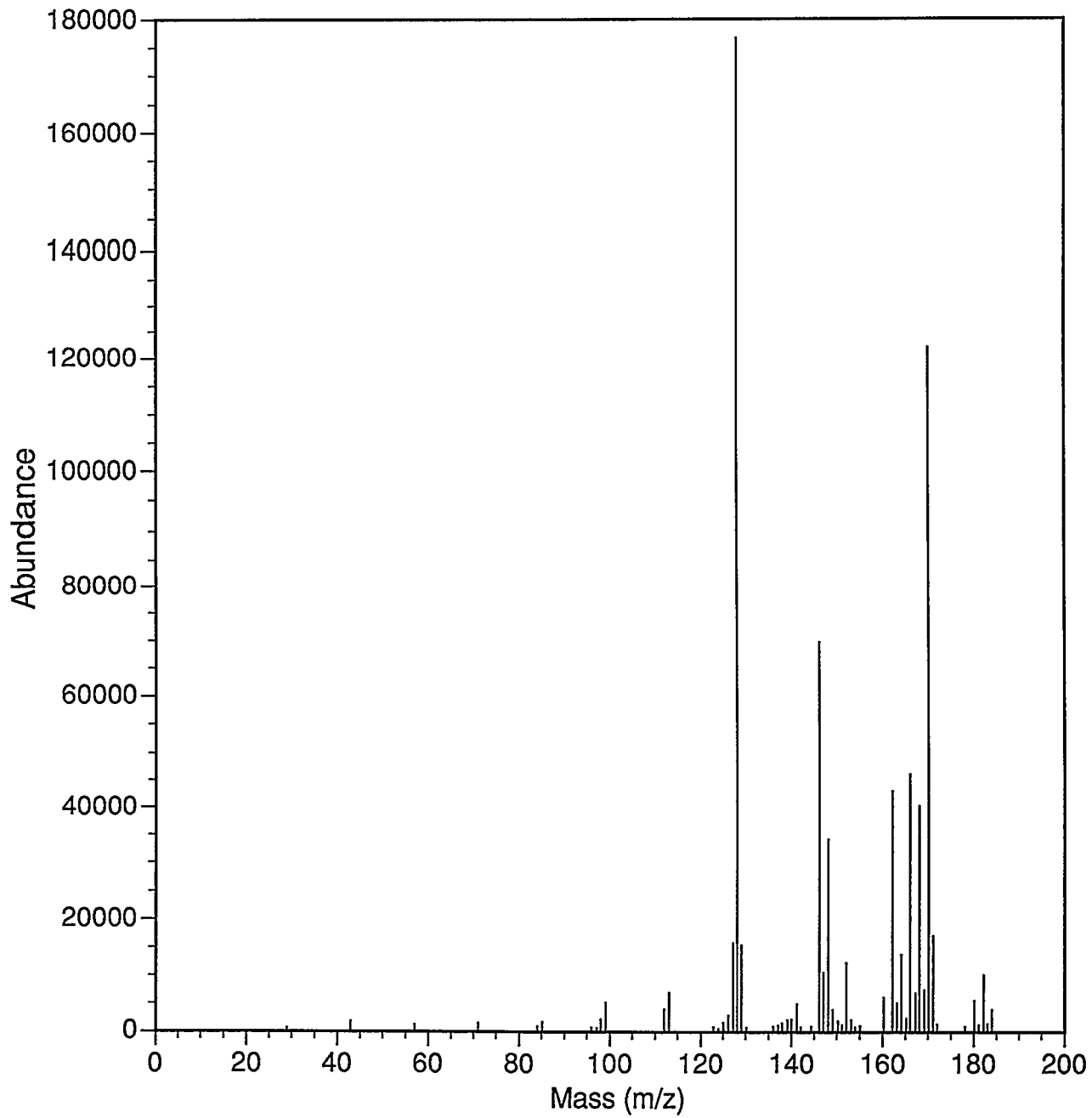


Figure 4. Mass spectrum recorded at 4.51 minutes for the JP-5 jet fuel shown in Figure 3(b).



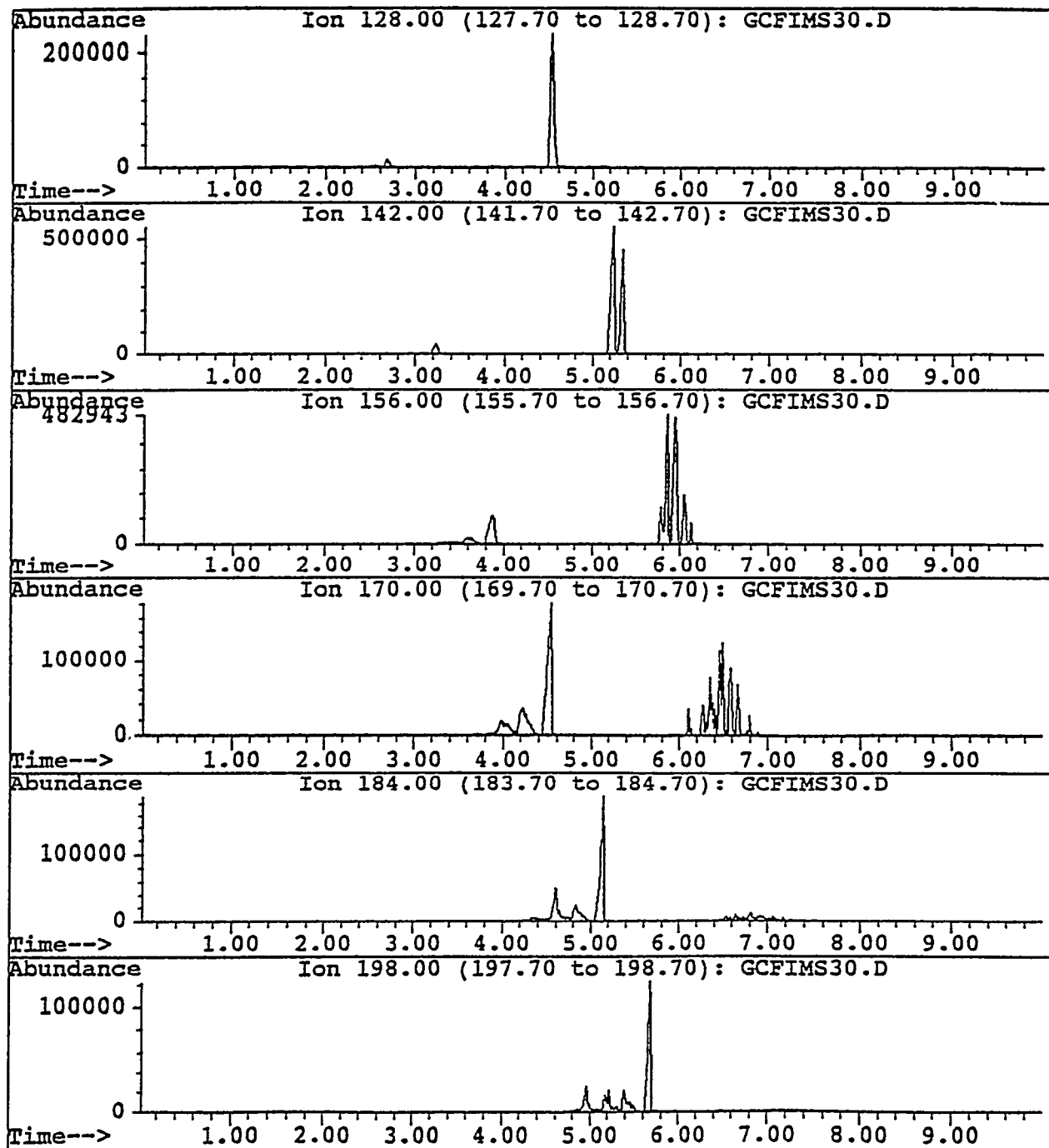


Figure 5. Ion chromatograms for the homologous series of acyclic alkanes and naphthalenes extracted from the TIC of the JP-5 fuel.

fuel and a decline in the naphthalenes. This switch is a natural consequence of the fact that because the boiling point of an acyclic saturate is lower than that for an alkylnaphthalene of the same mass, within a given boiling point fraction the higher molecular weight materials will be those that have higher vapor pressures.

Examination of these chromatograms shows that the time window of elution of a given hydrocarbon type increases with the molecular weight (i.e., complexity of the substitution pattern). In order to see if the time windows for isobaric acyclic alkanes and alkylnaphthalenes begin to overlap for higher molecular weight compounds, we examined the selected ion chromatograms from commercial diesel fuels. Diesel fuels tend to be higher boiling than jet fuels and cover a wider mass range. Figure 6 shows the retention time windows observed for the alkanes and the naphthalenes as a function of molecular mass. It would appear that there is more than adequate resolution between these classes, at least up to 282 Da.

### Z-Series Analysis

One convenient way to display the composition of a hydrocarbon fuel is by using a z-series table. The elemental formula of any hydrocarbon can be generally expressed as  $C_nH_{2n+z}$ , where z is a measure of the unsaturation index. All acyclic alkanes have the general formula of  $C_nH_{2n+2}$  (i.e., a z-value of +2), and monocyclic alkanes have the general formula of  $C_nH_{2n}$  (i.e., a z-value of 0). The z-value decreases by 2 for every degree of unsaturation (ring or double bond). In a z-series table the columns correspond to different z-values (i.e., compound type) and the rows correspond to different number of carbon atoms (i.e., molecular size). Thus, a z-series table gives the composition of a fuel by compound type and molecular size.

To extract a z-series table from the TIC involves the following steps: (1) extract ion chromatogram for a selected mass; (2) refer to appropriate time windows for integration; (3) apply appropriate correction for relative sensitivity to the integrated intensities and store result in the appropriate table entry; (4) repeat steps 1 through 3 for all the masses; and (5) normalize the table. Although relatively straightforward, it would be painstaking to perform these steps manually. We have therefore automated these steps by writing a program using HP's macro language, and have included it as an option in the "Chromatogram" menu of the standard MSD software. By examining selected ion chromatograms of various homologous series in different fuels, we have determined a set of time windows for each compound class. As for the sensitivity factors, they do vary with compound class, although their value within a compound class is reasonably constant.<sup>1</sup> For example, within the alkylbenzene class, the variation in sensitivity factor as a function of chain

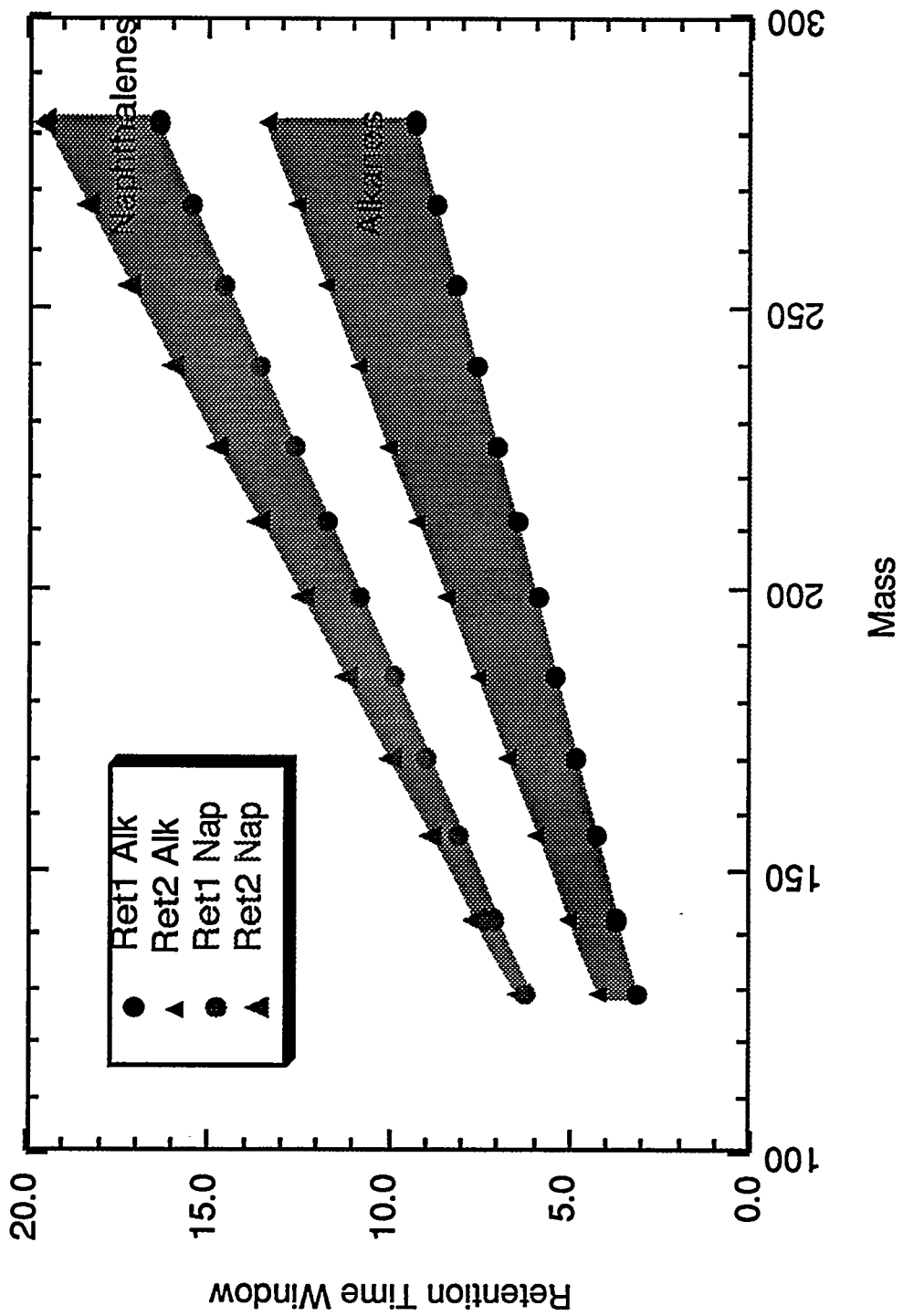


Figure 6. Retention time windows of acyclic alkanes and alkylnaphthalenes.

length is typically only  $\pm 15\%$ . On the other hand, the average sensitivity factor for the alkylbenzene class differs from acyclic saturates by almost a factor of five. In general, once these sensitivity factors are measured for a given volcano source using a calibration mixture, they will remain constant for extended periods of operation, thus allowing for rapid and accurate conversion of peak areas into absolute concentrations. We have assigned a set of sensitivity factors based on our analysis of test mixtures and our previous experience with FI. We are currently in the process of analyzing many different fuels that have been well-characterized by other techniques to obtain a set of self-consistent sensitivity factors.

Even though the time windows and sensitivity factors have not been finalized, we can get useful data from this technique. Figure 7 gives the results of such quantitative z-series analysis for a naphtha feed to a reformer. The analysis of the product is shown in Figure 8. As can be seen from these z-series tables, the feed consists mainly of acyclic and monocyclic saturates, and has very little aromatics. The product, on the other hand is rich in alkylbenzenes and other aromatics including some naphthalenes. With such detailed description one can know how the hydrogen is distributed in the product as well as pick up signs of catalyst deactivation. We believe that the ability to deliver this kind of information in less than fifteen minutes makes this method suitable for use in process monitoring and control.

## Summary

The preliminary results reported here clearly show the feasibility of using field ionization mass spectrometry in combination with gas chromatography for the rapid and quantitative analysis of refined hydrocarbon fuels. Numerous factors associated with the present GC-FIMS configuration have not been optimized during this initial effort. Foremost among these are the chromatography and the analysis software. Optimization of the chromatography is dependent on the exact application. However, multicolumn GC systems designed for hydrocarbon fuels analysis could readily be incorporated into a "next generation" GC-FIMS instrument.

The present HP analysis software provided with the MSD is extremely powerful and flexible. Naturally, however, it is designed to interpret data that is acquired from a standard 70-eV electron impact source. For optimal use, the type of data presented above requires a considerably different approach to analysis that is specifically tailored to both the ionization mechanism (FI), the sample characteristics (refined fuels), and the desired analytical results (grouped compound class information). The considerable simplification in the mass spectra provided by FI makes this type

z-Table

	2	0	-2	-4	-6	-8	-10	-12	-14
1									
2	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-
5	0.178	0.438	-	-	-	-	-	-	-
6	0.577	1.029	-	-	0.052	-	-	-	-
7	3.789	13.555	-	-	8.074	-	-	-	-
8	9.003	10.738	0.403	-	18.795	0.017	-	-	-
9	8.740	7.805	0.943	0.000	13.050	0.216	-	-	0.0
10	2.205	6.233	0.395	-	1.142	0.230	-	-	-
11	0.858	0.823	0.070	-	-	0.092	-	-	-
12	0.336	0.094	-	-	-	0.017	-	-	-
13	0.103	-	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-	-
	25.789	30.715	1.811	0.000	41.114	0.571	0.000	0.000	0.0

Figure 7. Z-series analysis of a naphtha feed to a reformer.  
 Note the predominance of acyclic and monocyclic alkanes and the absence of aromatics.

z-Table

	2	0	-2	-4	-6	-8	-10	-12	-14
1	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-
5	0.146	0.261	-	-	-	-	0.000	-	-
6	0.188	0.234	-	-	0.376	-	-	-	-
7	0.966	0.742	-	-	12.310	-	-	-	-
8	1.100	0.630	0.043	-	33.983	0.023	-	-	-
9	0.301	0.079	-	0.000	33.796	0.620	0.086	-	-
10	-	-	-	0.010	10.563	0.383	0.059	0.382	0.001
11	-	-	-	-	1.135	0.119	0.008	0.495	-
12	-	-	-	-	0.102	0.013	-	0.448	0.001
13	-	-	-	-	-	-	-	0.200	0.021
14	-	-	-	-	-	-	-	0.046	0.031
15	-	-	-	-	-	-	-	-	0.051
16	-	-	-	-	-	-	-	-	0.021
17	-	-	-	-	-	-	-	-	0.001
18	-	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-	-
	<u>2.701</u>	<u>1.946</u>	<u>0.043</u>	<u>0.010</u>	<u>92.265</u>	<u>1.158</u>	<u>0.153</u>	<u>1.570</u>	<u>0.15</u>

Figure 8. Z-series analysis of a naphtha product from a reformer.  
 Note the marked increase in aromatics and the absence of higher alkanes.

of software much easier to implement, and less prone to inaccuracies introduced by complex spectral subtractions.

The work summarized here clearly shows the utility of gas chromatography/field ionization mass spectrometry in general, and of the volcano-style field ionization source in particular. Although some additional development effort is required to optimize the chromatography and to automate the quantitation software, we have already demonstrated that GC-FIMS is a very powerful and unique analytical tool.

## REFERENCES

1. Malhotra, R.; Coggiola, M.J.; Young, S. E.; Tse, D. S.; Buttrill, S. E. Jr., "*Analysis of Middle Distillate Fuels by High Resolution Field Ionization Mass Spectrometry*," Final Report, Naval Research Laboratory, Contract No., N00014-81-K-2032, 1987.
2. Hazlett, R. N.; Hardy, D. R.; Malhotra, R., *Energy & Fuels* **1994**, *8*, 774.
3. See, for example, Karam, H. S.; McNair, H. M.; Lancas, F. M. "Characterization of Alternative Fuels by HPLC and GC-MS," *LC-GC* **1987**, *5*, 41.
4. Wadsworth, P.; Vilalanti, D. *Anal. Chem.* **1992**, *64*, 2227.
3. Aberth, W.; Spindt, C. A. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 183.





*6th International Conference  
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Vancouver, Canada  
October 12-17, 1997*

**STUDIES ON THE NATURE OF GUM FORMED IN CRACKED NAPHTHAS**

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**Abstract**

Cracked naphthas from fluid catalytic cracking (FCC) operations are generally the major blending components in gasoline. Naphthas from thermal cracking operations also find their ways in gasoline pool in some refineries. Composition of these two generic classes of naphthas, their gum forming tendencies and nature of gum formed have been studied. The soluble and insoluble gum have been characterised for functional groups by infra red (i.r.) spectroscopy and the molecular weight profile, using gel permeation chromatography. The nature of the gum is correlated with the composition of the naphthas.

Two FCC naphthas, two visbreaking naphthas and one coker naphtha were taken for the study. The FCC naphthas contain relatively higher levels of mono-olefins and conjugated diolefins with high branching. The thermal cracking naphthas have higher levels of  $\alpha$ -olefins and are abound in di, tri and cyclo-olefins.

The infrared spectra of gum produced under identical accelerated ageing conditions show that the hydroxyl functionalities in the gum from FCC and thermal cracking naphthas are of the same nature but hydrogen bonding in gums from thermal cracking naphthas are stronger. Carbonyl functionalities indicate formation of different types of esters in gum formed in naphthas from two different routes.

Molecular weight of both the soluble and insoluble gums are distributed from 140 to around 2000 in both types of naphthas. However, the distribution shows that the insoluble gums contain higher amount of high molecular weight polymers as compared to the soluble ones.

## **INTRODUCTION**

Refinery gasoline pool consists of streams from various secondary conversion processes besides the straight run naphthas. The secondary processes streams are generally from catalytic cracking, thermal cracking, reforming, isomerisation, alkylation, polymerisation etc. In the unleaded gasoline era the proportions of these streams have increased. The naphthas from thermal and catalytic cracking processes have poor stability due to hydrogen deficiency and tend to form gum through air oxidation, condensation and polymerisation during storage and handling. Peroxides are known to be intermediates in gum formation reactions. Gum formation causes serious problems in fuel system and intake system of the engine[6].

FCC naphtha is generally a major cracked streams while thermally cracked naphthas from visbreaking and coking operations are accommodated to a lesser extent in gasoline in some refineries. The gum formation tendencies of the cracked components are influenced with several physical parameters, but chemical composition (various olefin types) is of prime importance. The two different types of cracked naphthas have different composition and are varying in different types of olefinic structures and as such variation in gum forming tendencies. In the present study, composition of two generic classes of naphthas, their gum forming tendencies and the nature of the gum formed in accelerated aging conditions have been studied.

To gain information about the difference in quality of soluble and insoluble gums as well the gum obtained from FCC and thermal cracking naphthas, the gums generated through the accelerated test (ASTM D 873, 4 hrs, aging) have been characterised by infra - red spectroscopy and gel permeation chromatography.

## **EXPERIMENTAL**

Two FCC naphthas, two visbreaking naphthas and one coker naphtha collected from different operating refineries were characterised for various physico-chemical characteristics using standard test techniques[1]. Composition of these naphthas were determined by mass spectrometry, NMR and by a combination of olefin separation, hydrogenation and gas-liquid chromatography described elsewhere[3,4,5]. Soluble and insoluble gum produced in ASTM D

874 test (4 hrs aging at 100 psi oxygen pressure at 100°C) were taken for analysis through IR spectroscopy and gel permeation chromatography.

Infra-red spectra of soluble and insoluble gums were recorded on PE 1760X FTIR instrument controlled by PC-AT. The resolution used in these spectra was  $2.0\text{ cm}^{-1}$  and number of accumulations were 32. The background absorption was compensated using sample shuttle accessory which make the instrument effectively double beam. The samples were dissolved in  $\text{CH}_2\text{Cl}_2$  and thin films were prepared on KBr plates by spreading these solutions and evaporating the solvents. In few samples, Tetrahydrofuran (THF) was used to dissolve them. For comparison purpose the spectra of soluble and insoluble gums were overlayed on the same chart.

Water, Gel Permeation Chromatography (GPC) equipment with pump model 590 with U6K injector was used for the analysis. Column used was 100°A ultra styragel. THF solvent at 1.0 ml/min and RI detector was used for the analysis. The set-up is equipped with Mixima 820 chromatographic Data Station.

## **DATA AND DISCUSSION**

### **Characteristics,Composition of Cracked Naphtha**

Physico-chemical characteristics which are important from the fuel stability point of view are given in Table-1 and the chemical composition determined using different techniques are listed in Tables 2 and 3. Table 1 consists of the generally acceptable values of physico-chemical parameters for a stable gasoline[2] for the comparison.

Most of the available analytical techniques have limitations in analysing the cracked naphthas. To overcome these limitations, multiple techniques were used to get a meaningful information.

The aromatic content in cracked naphthas as determined by mass spectrometry range from 6.0 to 11.1 %vol. The magnitude of olefins in FCC naphthas are appreciably higher as compared to thermally cracked naphthas (55.1 and 52.4 %vol in FCC naphtha A and B respectively and 32.1

and 41.6 %vol in visbreaking naphtha A and B and in coker naphtha the olefin content is 41.6 %vol).

Mass spectrometry data shows that among the olefin types, mono-olefins are predominant in FCC naphthas (71.0 and 72.6 % vol of total olefins in FCC naphtha A and B respectively). The olefins in thermally cracked naphthas contain relatively higher amounts of olefin types grouped as cyclo-olefins and di-olefins and acetylenes (34.3 to 38.8 % vol). Relatively higher proportions of olefins grouped as tri-olefins and cyclo-di-olefins are present in the olefinic portion of the thermal cracking naphthas.

NMR analysis of the olefin concentrate separated from the naphthas shows that the thermally cracked naphthas contain higher amount of terminal double bond (alpha) olefins as compared to internal olefins. Alpha to internal olefin ratio in thermal cracking naphthas are between 1.11 to 1.33. While these values in case of FCC naphthas A and B are 0.73 and 0.75 respectively.

Iso- and normal olefin distribution was determined in the cracked naphthas by hydrogenation of olefins concentrate and g.l.c. analysis of hydrogenated product (Table-3). Like paraffin distribution, the FCC naphthas are rich in iso olefins also.

### **Comparison of Soluble and Insoluble Gum**

The FTIR spectra of the soluble and insoluble gums are presented in Figures 1 to 5 for the five cracked naphthas. Important band assignments are tabulated in Table-4.

Soluble and insoluble gums from both the FCC naphthas contain H-bonded hydroxyl functionalities. Soluble gum contains only one type of ester carbonyl ( $1710\text{ cm}^{-1}$ ) while there are two types of carbonyl functionalities ( $1740$  and  $1725\text{ cm}^{-1}$ ) in insoluble gum.

Both the gums from FCC naphthas contain olefinic structures ( $1640$  and  $1655\text{ cm}^{-1}$  in insoluble and soluble gums respectively). The concentration in insoluble gum being more as

compared to soluble gum. Methyl/methylene ratio of soluble gum is higher as compared to insoluble gum.

Both sediments from Visbreaking Naphthas contain same type of hydroxyl functionality ( $\sim 3400 \text{ cm}^{-1}$ ). Comparing relative intensities, these functionalities are much higher in insoluble gum as compared to the soluble gum, which is also supported by the presence of very strong band at  $1185 \text{ cm}^{-1}$ . As insoluble gums contain higher molecular size components which are formed due to condensation / polymerization through hydrogen bonding, H-bonded hydroxyl functionality could be higher in the insoluble gums. Only one type of carbonyl functionality is observed in soluble ( $\sim 1702 \text{ cm}^{-1}$ ) and insoluble ( $\sim 1710 \text{ cm}^{-1}$ ) gum. Olefinic contents are also present in both the gums. The positions of olefinic bands ( $\sim 1643 \text{ cm}^{-1}$  in insoluble gum and  $\sim 1625 \text{ cm}^{-1}$  in soluble gum) indicate the presence of some conjugated olefins in soluble gum which shifts the band to lower frequency. Methyl/methylene ratio in soluble gum is higher than that in insoluble gum.

In case of gum from coker naphtha, the bands at  $\sim 3448 \text{ cm}^{-1}$  and  $\sim 3400 \text{ cm}^{-1}$  in soluble and insoluble gums respectively, indicate the presence of highly H-bonded hydroxyl groups in insoluble gum, supported by the presence of strong band at  $\sim 1183 \text{ cm}^{-1}$  due to same reasons as explained in case of visbreaking naphthas. Only one type of ester carbonyl is present in soluble gum ( $\sim 1708 \text{ cm}^{-1}$ ) while two types in insoluble gum ( $\sim 1745$  and  $\sim 1708 \text{ cm}^{-1}$ ). Some types of olefinic structures (band at  $\sim 1632 \text{ cm}^{-1}$ ) are present in both the sediments; the relative concentrations being more in insoluble gum. Methyl/methylene ratio is higher in soluble gum than that of insoluble gum.

### **Comparison of Gum from FCC, Visbreaking and Coker Naphtha**

Hydroxyl functionalities in all the sediments from three types of naphthas are of same nature, but the hydrogen bonding is stronger in visbreaking and coker samples as compared to gums - from FCC naphthas. Their relative concentrations are also higher in visbreaking naphtha samples. This difference could be due to formation of more polar components formed due to autooxidation of di- and higher olefins, particularly conjugated one, which participate in H-bonding.

The carbonyl functionalities in sediments of thermally cracked naphthas are absorbing at  $1708\text{ cm}^{-1}$  while those in FCC, absorb at  $1720\text{--}40\text{ cm}^{-1}$  which indicate the different types of esters formed in naphthas from two different routes.

In all the naphthas, methyl/methylene ratios are higher in soluble gums as compared to insoluble ones which reveals that esters and hydroxyl containing molecules forming insolubles gums contain longer paraffinic chains and / or more naphthenic components as compared to those forming soluble gums.

### **Molecular Weights Distribution**

Only one column was used in GPC and so the molecular weight calculations are only approximate. Besides that the sample composition is of a varied nature and therefore, the detector response has to be analysed with limitations. However, the analysis should give a fairly good idea of molecular weights distribution, especially for comparing the samples with each other. One FCC naphtha - B and one visbreaking naphtha - B and the coker naphtha were studied for the molecular weight distribution of the gum formed in the naphtha after aging.

The molecular weight distribution data of the soluble and insoluble gum formed are given in Table-5. Weight average molecular weights of the insoluble gums from the three naphthas are invariably higher than the soluble gum (ranging from 912 to 935 while in the case of soluble gum the weight average molecular weight ranges from 606 to 839. However, in case of the number average molecular weight, although the similar trend is visible in FCC and visbreaking naphtha, the values are reverse in case of coker naphtha and thus the similar observations can be made from the value of polydispersity. Number average molecular weight ranges from 449 to 612 for soluble gum and for insoluble gum the variation is from 581 to 610.

Molecular weight of both the soluble and insoluble gums are distributed from 410 to around 2000 or marginally above 2000 but from the distribution it is quite clear that the insoluble gums contain higher amounts of high molecular weight polymers as compared to the soluble gums.

## CONCLUSION

Chemical composition of naphtha sample through mass spectrometry shows that FCC naphthas have substantially higher olefins than thermally cracked naphthas. The FCC naphthas are predominant in mono-olefins (72.6 to 71.0 % vol of total olefins) and have higher iso to normal ratio. The olefins in thermally cracked naphthas have relatively higher proportions of olefins grouped as cyclo - olefins + di-olefins + acetylenes ranging from 34.3 to 38.4 %vol of the total olefins as compared to FCC naphthas (25.6 and 28.6 %vol) Relatively higher proportions of olefins grouped as tri-olefins + cyclo di-olefins are found to be present in thermal cracking naphthas. The thermal cracking naphthas also contain relatively higher alpha olefins.

Although the olefin content in thermal cracking naphthas are much lower than in FCC, the potential gum in thermal cracking naphthas are quite high and is maximum in case of coker naphtha. This is due to relatively higher proportions of di and tri olefins and acetylenes in these naphthas.

FT ir spectras of the soluble and insoluble gums from the cracked naphthas show that carbonyl and to olefinic functionalities are generally, stronger in insoluble gum. However, the methyl / methylene ratios are higher in soluble gum. The gums from thermally cracked naphthas have strong hydroxyl functionality particularly from coker naphtha. This again due to higher autooxidation tendencies of di- and tri- olefins predominant in this naphtha.

The molecular weight profile as studied with gel permeation chromatography shows that the average molecular weight of the insoluble gums are invariably higher (912-915) as compared to the soluble gum ranging from 606 to 839.

## ACKNOWLEDGEMENT

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## REFERENCES

1. Annual Book of ASTM Standards - Petroleum Products, Lubricant and Fossil Fuels” American Society of Testing Materials 1995, Easton MD, USA.
2. Schrepfer M.W., “Chemical Treating Technology Ensures the Quality and Performance of an Automotive Fuels”, Australian Fuel Quality Symposium, Petrotech 88, Melbourne, March, 1988.
3. Fink D.F., Lewis R.W. and Weiss F.T., Analytical Chemistry 1950, 22 (7) p. 850.
4. Fink D.F., Lewis R.W. and Weis F.T., Analytical Chemistry 1950, 22 (7) p. 858.
5. Nagpal J.M., Joshi G.C., Moolchandra E. And Rastogi S.N., “Analysis of Olefinic Structure in Cracked Naphtha through Catalytic Hydrogenation and Capillary GLC Technique”, Proceedings of IXth National Symposium of ISAS, New Delhi, December 22-24, 1992.
6. Tseregounis S.I., SAE Paper No. 881641, 1988



Table - 1

CHARACTERISTICS OF CRACKED NAPHTHAS AND GENERALLY ACCEPTABLE VALUES FOR GASOLINE

Test	Acceptable Values	FCC Naphtha		FCC Naphtha		VB Naphtha		Coker Naphtha	
		A	B	A	B	A	B	A	B
Hydrogen Sulphide	< 1 wt ppm	ND	ND	227.0	ND	ND	ND	ND	ND
Mercaptan Sulphur	<5 wt ppm	269	0.8	3980	3.3	396.0	3.3	396.0	3.3
Thiophenols	< 1 wt ppm	7.8	ND	32.0	ND	ND	ND	ND	ND
Peroxiide No.	< 0.5	4.8	5.0	1.0	2.7	3.6	2.7	3.6	2.7
Existant Gum	< 2mg/100 ml	5.8	78.3	3.4	6.8	0.8	6.8	0.8	6.8
4 Hours Accelerated Gum	< 5mg/100 ml	721.1	364.2	719.3	517.6	886.2	517.6	886.2	517.6
Induction Period min.	> 300 Min.	104	22	39	108	131	108	131	108
Free Sulphur ppm	< 1wt ppm	ND	ND	ND	ND	ND	ND	ND	ND
Copper, ppm	<10 wt ppb	<10	<10	<10	<10	<10	<10	<10	<10
3 Months Storage Stability at 43°C mg/100 ml	4 mg/100 ml	165.4	232.7	134.7	126.4	42.6	126.4	42.6	126.4
Density kg/litre at 15°C	-	0.7143	0.7067	0.7273	0.7240	0.7140	0.7240	0.7140	0.7240
Distillation Data, °C, ASTM D86 IBP/50%/FCC	-	45/83/155	47/82/144	51/107/152	48/114/183	55/92/163	48/114/183	55/92/163	48/114/183

Table - 2

## MASS SPECTRPOSCOPY ANALYSIS OF CRACKED NAPHTHAS

% Vol	FCC	FCC	VB	VB	Coker
	Naphtha	Naphtha	Naphtha	Naphtha	Naphtha
	A	B	A	B	
Paraffins	26.2	32.2	42.9	46.1	39.8
Monocyclo - Paraffins	7.2	9.0	17.8	11.1	11.4
Dicyclo-Paraffins	0.4	0.1	0.0	0.9	0.2
Mono Olefins	40.0	37.2	18.9	21.1	24.8
Cyclo - Olefins + Diolefins + Acety - lenes	14.1	15.0	11.0	13.8	14.9
Triolefins + Cyclo- diolefins	1.0	0.2	2.2	1.0	1.9
Benzenes	11.1	6.3	7.2	6.0	7.0
<b>Olefins Distribution, % Vol of total Olefins</b>					
Mono - olefins	72.6	71.0	58.9	58.8	59.6
Cyclo - olefins + Diolefins + Acetylenes	25.6	28.6	34.3	38.8	35.8
Tri - olefins + Cyclo- diolefins	1.8	0.4	6.8	2.8	4.6
<b>Total</b>					
Paraffins	33.8	41.3	60.7	58.1	51.4
Olefins	55.1	52.4	32.1	35.9	41.6
Aromatics	11.1	6.3	7.2	6.0	7.0

**Table - 3**  
**NMR SPECTROSCOPY AND GLC ANALYSIS DATA OF**  
**CRACKED NAPHTHA SAMPLES**

<b>% Vol</b>	<b>FCC Naphtha</b>	<b>FCC Naphtha</b>	<b>VB Naphtha</b>	<b>VB Naphtha</b>	<b>Coker Naphtha</b>
	<b>A</b>	<b>B</b>	<b>A</b>	<b>B</b>	
Ratio of Alpha to internal olefins (NMR)	0.73	0.75	1.30	1.33	1.11
<b>Analysis of Olefins (Separated by Colum Chromatography) by Hydrogenation and GLC Analysis</b>					
iso-Olefins	49.8	50.3	36.1	37.3	28.6
n-Olefins	24.0	21.9	30.0	31.3	43.6
Cyclic Olefins	24.3	27.7	30.1	22.2	26.5
Unknown + C <sub>9</sub>	1.9	0.1	2.8	9.2	1.3

Table -4  
**IMPORTANT BAND ASSIGNMENT IN FTIR SPECTRA OF SOLUBLE AND INSOLUBLE GUM FROM CRACKED NAPHTHAS**

Band Assignment	FCC Naphtha A		FCC Naphtha B		VB Naphtha A		VB Naphtha B		Coker Naphtha	
	Soluble gum	Insoluble gum	Soluble gum	Insoluble gum	Soluble gum	Insoluble gum	Soluble gum	Insoluble gum	Soluble gum	Insoluble gum
OH	3433	3421	3457	3444	3397	3399	3404	3393	3448	3400
C-H	2929	2926	2947	2922	2926	2961	2959	2925	2960	2929
	2872	2855	-	2854	2855	2930	2929	2855	2929	2854
	-	-	-	-	-	2874	2872	-	2872	-
C=O	1705	1740	1735	1742	1702	1711	1705	1709	1708	1707
	-	1721	-	-	-	-	-	-	-	-
C=C	1655	1646	1641	1640	1621	1643	1626	1646	1632	1631
$\beta$ CH <sub>2</sub>	1457	1457	1457	1457	1460	1454	1457	1453	1458	1447
$\beta$ CH <sub>3</sub>	1378	1379	1376	1378	1378	1382	1378	1376	1378	1375
C-O	1167	1168	1165	1166	1230	1185	1167	1181	1166	1183
	1000	1048	-	-	1166	1055	1129	1035	1029	1097
	-	-	-	-	1035	1023	1036	-	-	1026

**Table - 5**  
**MOLECULAR WEIGHT DISTRIBUTION OF SOLUBLE AND INSOLUBLE GUM GENERATED IN CRACKED NAPHTHAS**  
**BY ASTM D873, 4 HRS.**

Gum from Cracked Naphtha	Number Av. Molecular wt.	Weight Av. Molecular Weight	Poly Dispersity	Molecular Weight Distribution Area %				
				> 2000-1500	1500-1000	1000-500	500-250	<250
<b>FCC Naphtha B</b>								
Soluble gum	449	606	1.35	0.89	15.81	38.50	34.02	10.78
Insoluble gum	610	915	1.5	18.64	25.35	28.71	21.75	5.55
<b>VB Naphtha B</b>								
Soluble gum	511	769	1.50	6.48	28.87	32.45	20.45	11.75
Insoluble gum	581	935	1.61	16.42	24.99	29.08	24.01	5.50
<b>Coker Naphtha</b>								
Soluble gum	612	839	1.37	9.65	29.69	33.88	24.23	2.55
Insoluble gum	582	912	1.57	16.48	33.70	20.66	20.57	8.59

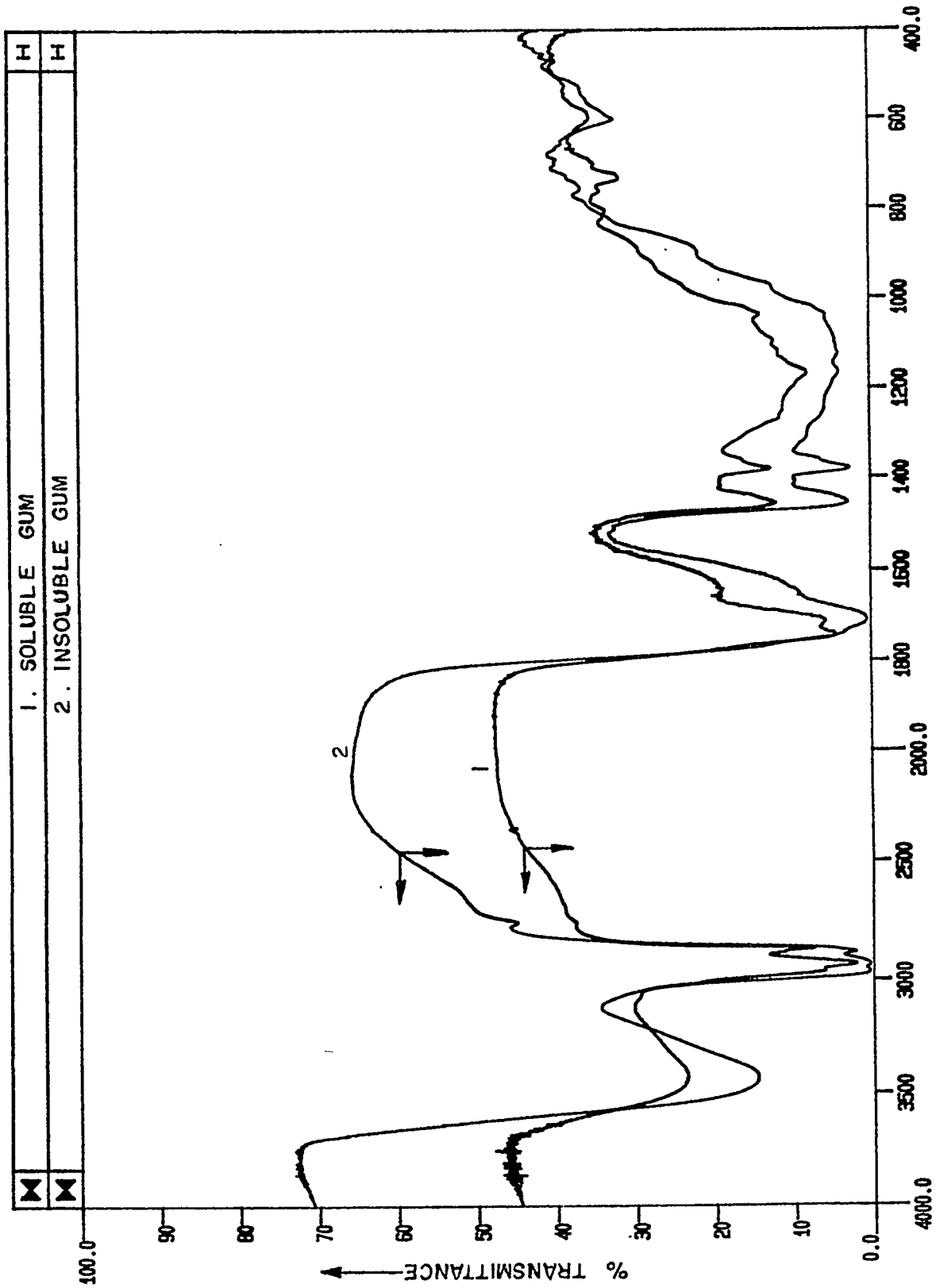
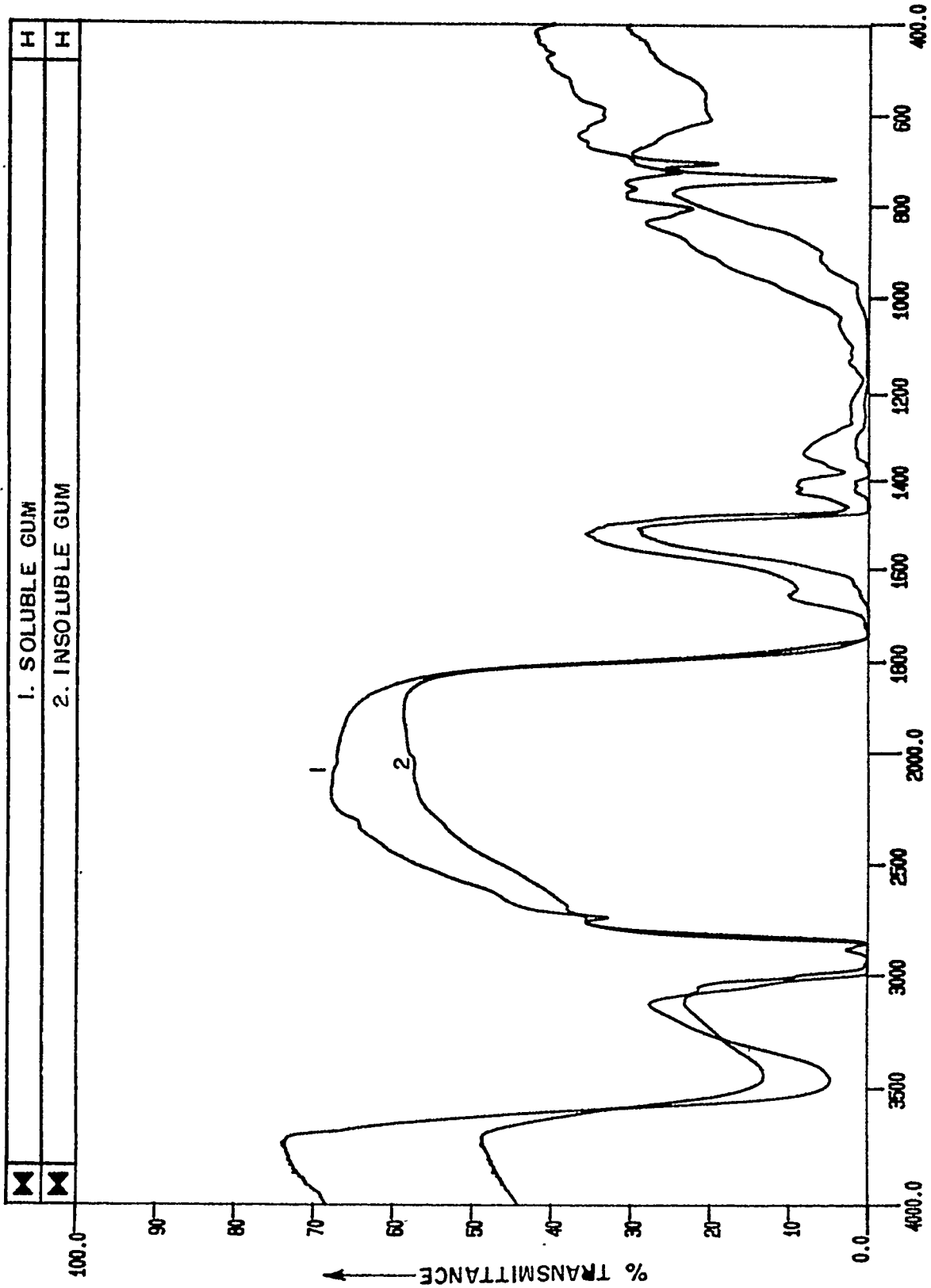


FIG. I : FT IR SPECTRA OF FCC .NAPHTHA A GUM



WAVE LENGTH CM-1 →  
 FIG. II : FT IR SPECTRA OF FCC NAPHTHA B GUM

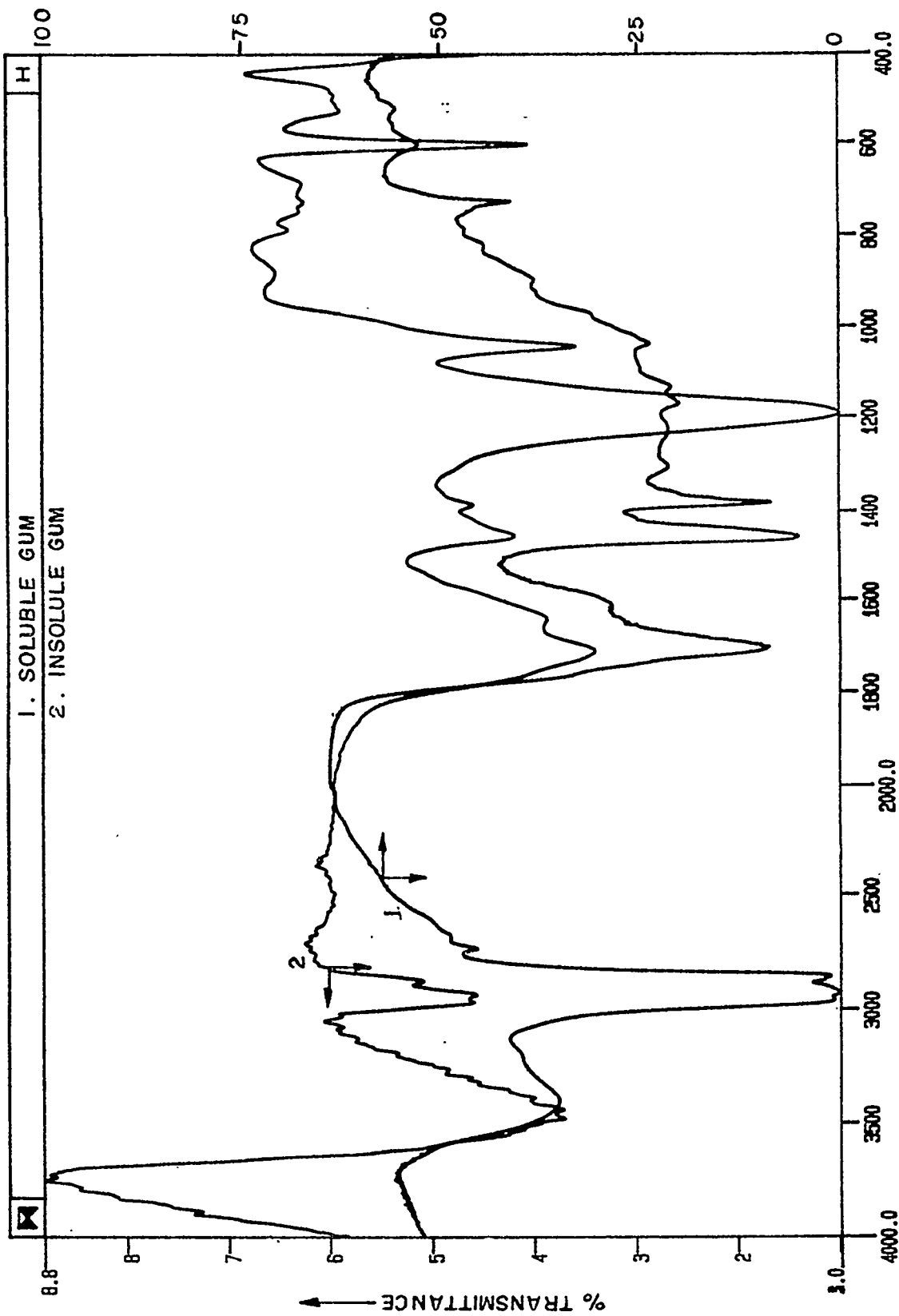


FIG. III : FT IR SPECTRA OF VB NAPHTHA-A GUM.



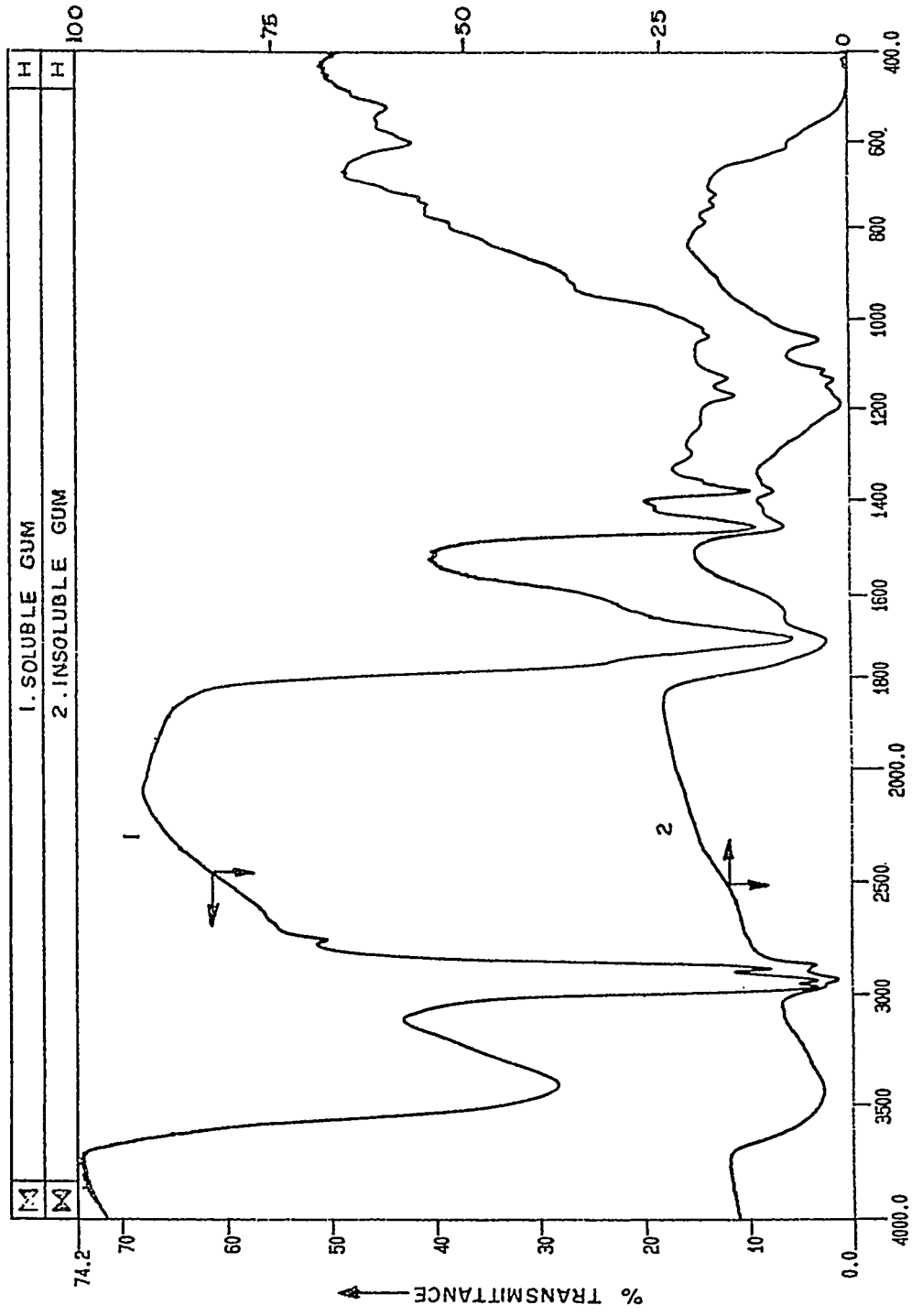


FIG. IV : FT IR SPECTRA OF VB NAPHTHA B GUM

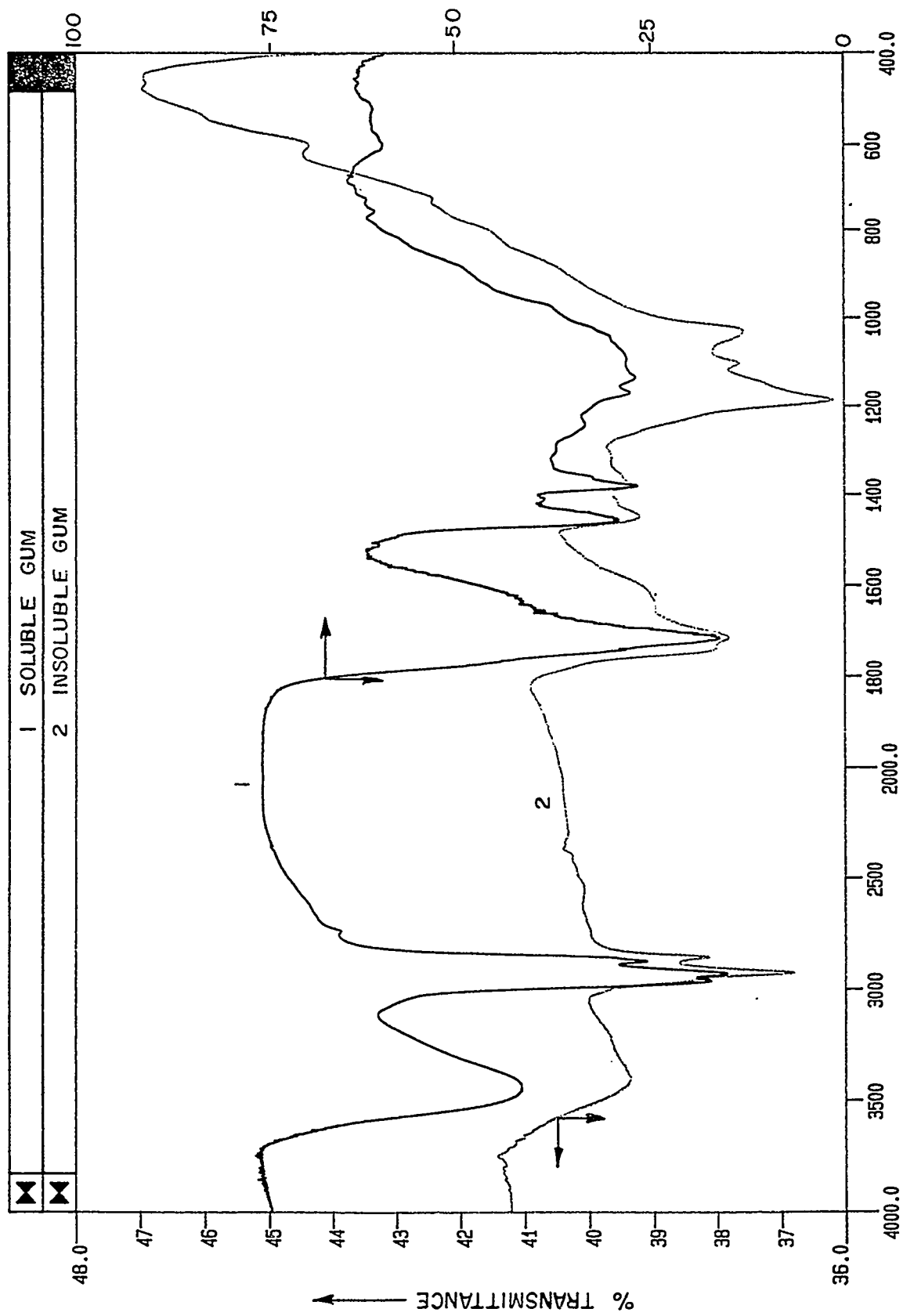


FIG. V : FTIR SPECTRA OF COKER NAPHTHA.GUM

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AN EXPERT SYSTEM TO PREDICT FALL-OUTS FROM CRUDE OIL IN STORAGE

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ABSTRACT:

Crude oil in storage may exhibit fall-out phenomena. Heavy emulsion sludge, often formed by sea water, waxes and asphaltenes, appears at times. In other cases, heavy asphaltene rich gatch, sometimes oxidized, and unorganics, often held in heavy emulsion, are noticed. These changes will usually have detrimental results, which frequently are followed by severe economic loss. A well established theory on the causes and affecting factors of crude fall-out does not exist today. However, extensive data and long time experience, has been collected and documented by several storing organizations. An expert system, called EQPS, to predict deterioration of oil products, is in operation a number of years in Europe. In the present paper we wish to apply EQPS established technology to the problems of crude storage. Our aim in this presentation, is to exhibit a framework for a crude expert system. The assessment is based on related factors, such as the source of the crude, its producing and transportation methods, storage conditions, climatic influences and time in storage. The logical structure and reasoning patterns, for products are very similar to those of crude. The presented demonstration module is not based on actual data and real collected experience. The framework however, could turn into a real system, by collecting the relevant knowledge base from storing entities, and compiling it into the suggested system.

1. CRUDE OIL:

Both crude oil and oil products are most of the time a complex blend of numerous chemicals created by nature from biomass and/or produced artificially by man. These mixtures in crude oil are normally very compatible but handling or by-blends may disturb the balance, and make it incompatible. In these cases, deblending or gravity segregations of groups of chemicals or fall-outs of single type chemicals, may occur.

The reasons for this can be very numerous and can possible be traced to the producing, manufacturing, handling, treating and/or storing conditions.

A comprehensive theory of fall-out from crude, syncrudes or crude-product blends is not available and while experience is available it is incomplete.

While the topic in this paper is fall-outs from crude, let us briefly show that finished oil products are also not free from such problems. Oil experts know that gum and/or unorganic contaminants (including water) may fall out from gasolines. Solids and water may also fall from middle distillates. Here the main problem is a wax crystallization, forming molecules too heavy to stay in suspension. Through ageing byproducts rich in sulfur, nitrogen and oxygen which may deposit also.

Although theoretically, all the product typical fall-outs can occur in crude oil, the main issues are the fall-out formation of heavy emulsions mainly with sea water (or brine), waxes and asphaltenes and heavy oil components. Gatch formation often rich in asphaltenes caused by gravity segregation and helped by unorganics, may also occur. Sometimes, even microbiological processes may take place at tank bottoms.

The fall-outs from products are normally quite predictable - sometimes controllable by additives, as most are caused by temperature shocks or natural ageing processes, less often by deblending of incompatible product components. For the prediction of ageing processes in oil products there is an expert system called EQPS which is used by compulsory/strategic storage organizations in Europe. EQPS has been presented at the last IASH conference meeting in Rotterdam [4], [5]. The technology contained in this system, is to a large extent applicable also to the prediction of fall-outs from crude.

The sludging of crude however is more or less still a black box. Sometimes it is known that under certain conditions fall-out occurs, but the reasons why it happens and to what extent it can happen are not well understood. With natural crude oils simple deblending is rare, certain physical/chemical conditions/reactions must play a role, possibly also some microbiology. Extensive data collection has occurred in Japan with JNOC and much documentation of results has been done. Ingenious devices have been developed and are being applied to facilitate reblending of sludge, such as tank mixers, robots stirring the sludge etc. Refiners are also partly knowledgeable as they have to clean up crude tanks prior to inspection and repair, though the reason why the problems occur can hardly ever be given. This is true with tank cleaning companies also.

The SPR of USA has similar data experience and possibly also some reason/theory knowledge on sludge formation in salt caverns. NIPER has published since many years,

experience reports on this. Some cavern data may also come from Manosque in France, and some possibly from east European countries.

## 2. THE IDEA OF AN EXPERT SYSTEM:

An expert system is a computer program that encapsulates specialist knowledge about a particular domain of expertise. It should be capable of making intelligent decisions within its domain. Such a system is a simulation of the human expert knowledge and his way of reasoning.

In general, an expert system contains three main components:

1. The knowledge base.
2. The inference engine.
3. The user interface.

The knowledge base consists of facts, assertions and rules that summarize the field of expertise. PROLOG - a special declarative-logical programming language which have been developed for this purpose allows convenient expression of the knowledge base as a set of logical rules [8]. Unlike conventional data bases which are normally passive, an expert system tries actively to derive logical consequences from the set of rules. In case of partial information, the system attempts to fill in the gaps. An expert system should be able to "think" creatively. 'Thinking' is done by the inference engine, which supplies the system with reasoning capabilities. This component generates a 'line of reasoning' leading from known facts (input data) to logically consistent conclusions.

The user interface is the channel of communication between the user and the program. This component allows the user to enter data into the program in a simple manner and displays the system's conclusions and decisions in a clear and intelligible form.

An expert system should have a sort of 'growing' capability. As time passes, new information, knowledge and experience are usually acquired. These are incorporated, automatically or manually in the system. As a result, the system improves, and it's predictions become more accurate. Thus an expert system is viewed as a dynamic body of knowledge and experience, which could give up to date expert advice to the user.

The oil industry has seen many applications of expert systems in recent years. Often the precise mathematical modeling is impossible due to lack of knowledge about the functional relationship between influencing variables (parameters). At times, the mathematics would get

to complex for an efficient solution of such a model. In these situations, the technique of "expert system" proved valuable. The basic idea is that experts know from experience that certain things will happen under certain conditions, but cannot fully explain why they happen. This experience could be logically formulated, and combined with sound scientific knowledge, to produce a useful and valuable system. For in depth information on expert systems, the reader is referred to [7]. Many other good texts are available.

As was said earlier there is considerable experience with expert system prediction technology. The ACOMES group of European stock entities uses an ageing prediction system for gasoline, diesel/heating oil and jet fuel since 1993. Development was by a team of experts from the German Strategic Petroleum Reserve (EBV) and the Israel Institute of Biological Research (IIBR). In the course of development, 15 international experts from the US, Europe and Israel injected their knowledge on ageing processes. This system now prides itself on being able to predict product stability for 10 years ahead in both caverns and above ground tanks [4], [5].

Based on this encouraging experience we attempt to demonstrate in this manuscript, how an EQPS-type crude sludge module may work.

### 3. DESIGN CONSIDERATIONS:

Oil assessments and evaluations are based on many potentially influencing parameters. If the number of parameters gets very large, the assessment of a wide ranging experience with such parameters is beyond the capability of a human brain to handle quickly. Here the logical algorithm, using structured decision trees, which was developed for the EQPS system can help [6]. In the following we would like to show how such an expert system can be applied for the prediction of fall-outs from crude oil.

Let us briefly look at some major factors (parameters), which most likely need to be taken into consideration when trying to predict sludging. No doubt the source of crude is important with the chemical/physical crude characteristics, but also the production methods (e.g. water injection/ chemical additives/microbiology to enhance the yield of recovery etc.)

When blending crude in terminal/refinery tanks contamination with tank bottoms and - most important - storing incompatible crudes (naphthenic with paraffinic for instance) plays a major role.

The mode of transportation is sometimes important too, especially when the tanks were not cleaned and blending occurred in pipelines. Storage types like rock caverns, salt caverns or above ground steel tanks are major factors to consider. Possibly the most important factor is the individual storage conditions ranging from existing bottom sludge serving as fall-out nucleus over climate (temperature shocks, average temperature), maintenance to microbially induced chemical reactions, and finally of course the time in storage. This list is by no means complete and needs to be researched for a real project.

Data and logic are for demonstration only and represent so far little real expert experience. The latter has to be provided by a user organization when a real system is being built. Thus we employ dummy data only. A real system would be useable for emergency stock entities of the US, Japan, Germany and the Netherlands who have voiced interest, though also other countries storing large crude volumes like Korea, India etc. may find it useful.

This demonstration system is for above ground tanks, it could however be modified to cover also cavern storage. The demonstration as well as a real system would use about 80% of existing EQPS technology in the mathematical as well as data handling parts.

#### 4. INPUT PARAMETERS:

The first design step for building a sludge prediction system would be the identification of all relevant parameters. A potential list will be shown in Table 1. Parameters which influence sludging have to be quantified by assigning classification ranges, which express (sludging) risk factor indicated by each parameter. As in EQPS we choose to classify parameters into three categories 'high', 'medium', and 'low'. A quantitative parameter like '*Free Water in Oil*', is measured in ppm and a value between 0 and 100 will be rated as low risk for sludging. A value between 100 and 2000 poses a medium risk, whereas a value between 2000 and 5000 indicates high risk. A qualitative parameter like '*Climate Shocks*' poses low risk if there are no climate shock, a medium risk, if about on climate shock a year is expected, and high risk for sludging whenever shocks are frequent.

As mentioned earlier the parameters and their ranges are merely for the demonstration.

Table 1: Parameters Potentially Influencing Crude Sludge Formation:

Type of Test	Units	Method	Expert System Ranges			
			< low >	< medium >	< high >	
Sludge Found <sup>1</sup>			none	some	a lot	
Sludge Stirred <sup>2</sup>			none to stir	untouched	yes	
Age	years		0	1	3	40
Rough Climate			modest	cold winter only	extreme	
Climate Shocks			none	rare (once a year)	frequent	
Large Vessels			VLCC	MCC	GP	
Pipeline			none	short P/L	long P/L	
Coaster <sup>3</sup>			none	short voyage	long voyage	
Closed/Open			closed	partial	open	
Status (physical)			neat	deposits & corrosion	poor condition	
Below Above Ground			below <sup>4</sup>	partially buried+float	above ground <sup>5</sup>	
Status (Microbial) <sup>6</sup>			none	some	heavy	
Warming Status			permanent	occasional	unheated	
Unorganic Particulates	ppm		0	200	800	5000
Oil-Salt Content	ppm		0	20	60	1000
Emulsions in Oil		visual	none	some	a lot	
Free Water in Oil	ppm		0	100	2000	5000
Pump Turbulence			none	some	constant	
Robot Stirring			permanent	intermittend	never	
Thermal Move (temp. gradient)			significant	some	none	
High Metal Crude	Grade		Grade 1	Grade 2	Grade 3	
New Facilities			none	some	total	
Syncrude			none	some in blend	total	
Danger Blend Rating			Rating A	Rating B	Rating C	
Aged + Virgin Crude			all virgin	some old in blend	> 50% old	
API of Crude	scale		light	medium	heavy	
Pour Point of Crude	°C		-20	0	5	30
Wax Content of Crude (parafines)	%wt		0	40	60	80

<sup>1</sup> previously in filled tank and removed

<sup>2</sup> not removed, more sludge fallout

<sup>3</sup> local, broken traffic

<sup>4</sup> rock cavern

<sup>5</sup> steel and concrete

<sup>6</sup> at oil/water interface



Asphalt Content of Crude	%wt	0	10	30	60
Yield of Crude Long Residue	%wt	0	30	50	90
Yield of Crude Vac. Residue	%wt	0	10	20	40
Yield of Crude Light Dist.	%wt	70	50	30	0
Yield of Crude Kero	%wt	15	10	6	0
Yield of Crude Naphtha	%wt	40	25	15	0
HFO Asphaltene Content	%wt	0	2	8	20
HFO Aromatics	%wt	0	5	10	20
HFO Nickel (NI) 950°C+	ppm	0	30	60	100
HFO Vanadium (VA) 950°C+	ppm	0	50	200	1000
HFO Iron (Fe) 950°C+	ppm	0	50	100	1000
Yield VGO Vacuum Gasoil 370-530°C	%	0	10	20	40
VGO Pour Point (30-530°C)	°C	0	40	60	100
VGO Wax Content	%	0	5	30	90
Middle Distillates Kero Yield	%wt	50	30	10	0
Middle Distillates Wax Content-parfines	%wt	0	5	30	90
Gravity d 15 (300-370°C)	t/m3	0	.830	.840	1.00

##### 5. FLOW DIAGRAMS:

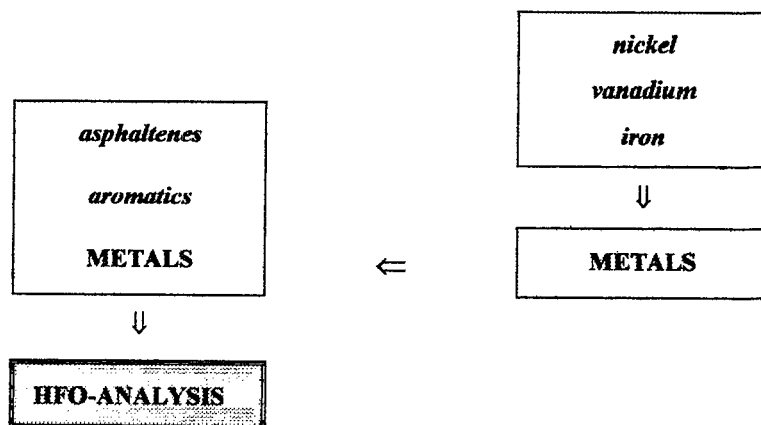
Then the parameters have to be logically structured into 'relevance' groups, called functions, exhibiting, according to experts, a sludging risk factor. For example, 'HFO-ANALYSIS' function is defined as such an aggregated sludging factor. It is based on '*HFO Asphaltene Content*' and '*HFO Aromatics*', both measured in %wt, and also on 'METALS'. The latter is itself a function based on three measurements: '*HFO Nickel (NI) 950°C+*', '*HFO Vanadium (VA) 950°C+*' and '*HFO Iron (Fe) 950°C+*'. Thus, the assessment of the 'METALS' function will be an input to the 'HFO-ANALYSIS' function, as shown schematically in Figure 1.

The assessment of function such as 'METALS' will be done by a decision tree, which will assign to each possible combination of 'high' 'medium' and 'low' (resulting from the classifications of the three metal measurements) an appropriate classification. The assignments are made by the crude oil experts, but could be modified by the user, to allow upgrading of the system, following newly gathered experience. The overall tree structure is summarized in three diagrams depicted in figures 2-4. Each diagram is a reasoning process of successive tree decisions leading to an assessment of a phase in the final decision. Memory

storing and processing of tree structures is handled by a special algorithm designed for EQPS [4], [6]. The three components of the final decision are called 'CONDITIONS', 'PHYSICALS' and 'CHEMICALS'. Experts prescribe to each combination of phase assessments a final decision. If for instance in a specific case, 'PHYSICALS' and 'CHEMICALS' are both rated 'low' (risk), and 'CONDITIONS' is rated 'high', the following text will be retrieved by the system:

*"Tankage conditions and handling are or were not desirable, though incompatibility problems seem to be low and the crude does not seem to be a risky one judging from its chemical composition. It is therefore unlikely that sludge problems will occur, at least not in the first 3-4 years."*

Figure 1: Reasoning Path for 'HFO-ANALYSIS'



#### 6. ASSESSMENT EXAMPLE:

Let us define the following example: A Libyan light crude of average age delivered by a large VLCC vessel followed by pipeline transport, was pumped into a partly buried underground crude tank.

The tank contained some sludge from a previous fill and sizable corrosion. The tank content will be circulated occasionally through 2 high sheer pumps. The crude was a syncrude type with byblends of 10% naphtha and 25% distillate cut. The crude is low on metals but contains a lot of wax. The climate in the tank's vicinity is extreme. More details on data crude characteristics are shown by the following table.

We show a listing of all the relevant sludge formation influencing parameters. Shaded areas display input values. On the right side of the input value, the risk level assigned by the

system, is shown. Functions (written in capital letters) and their assessments are both framed. The main phase (function) assessments are double framed.

CRUDE OIL EXPERT SYSTEM EVALUATION

Samples taken at 14/10/97 Tank No 81  
 Product: *crude* Location: *Crudenberg* Owner: *Oil Storage Inc.*

<u>TEST</u>	<u>VALUE</u>	<u>LEVEL</u>	<u>TEST</u>	<u>VALUE</u>	<u>LEVEL</u>
Below/Above Ground	partial	medium	Status (Physical)	corrosio n	medium
Warming Status	none	high	Status (Microbial)		-?-
<b>PROTECTION</b>	⇒	high	<b>CLEANLINESS</b>	⇒	medium
Closed/Open	open	high	Large Vessel	VLCC	low
<b>CLEANLINESS</b>		medium	Pipeline	short	medium
<b>PROTECTION</b>		high	Coaster	none	low
<b>TANK</b>	⇒	high	<b>TRANSPORT</b>	⇒	medium
Age	2	medium	<b>CLIMATE-AGE</b>		high
Rough	extrm.	high	<b>TRANSPORT</b>		medium
Shocks	rare	medium	<b>TANK</b>		high
<b>CLIMATE-AGE</b>	⇒	high	<b>ENVIRONMENT</b>	⇒	high
Sludge Found	some	medium	<b>CONDITIONS</b>	⇒	medium
Sludge Stirred	no	medium			
<b>ENVIRONMENT</b>		high			
Syncrude	some	medium	High Metal Crude	Grade 1	low
Danger Blend	A	low	<b>INCOMPATS</b>		

**Aged+Virgin Crude**

**INCOMPATS**          =>      **medium**

**Pump Recycle Turbulence**      some      **medium**

**Robot Stirring**

**Thermal Move**

**STRAIN-SHEER**          =>      **medium**

**NUCLEAR**                      **medium**

**STRAIN-SHEER**                      **medium**

**CATALYTICS**                      **low**

**Kerosene Yield**              **24**      **medium**

**MD Wax Content**              **89**      **high**

**D15 300-370°C**              **0.833**      **medium**

**MIDDLE DISTILLATES**          =>      **medium**

**MIDDLE DISTILLATES**              **medium**

**VGO**                              **medium**

**DISTILLATES**                  =>      **medium**

**Yield of Long Resid.**          **27**      **low**

**Yield of Vacuum Resid.**      **16**      **medium**

**New Facilities**

**CATALYTICS**                  =>      **low**

**Salt Content**                  **12**      **low**

**Emulsions**                      **none**      **low**

**Free Water**                  **2500**      **high**

**WATER-SALT**                  =>      **medium**

**PHYSICALS**                  =>      **medium**

**Yield**                              **3**      **low**

**Pour**                              **63**      **high**

**Wax**                               **32**      **low**

**VGO**                               =>      **medium**

**Crude Light Dist.**              **42**      **medium**

**Crude Kerosene**              **13**      **low**

**Naphtha Yield**               **30**      **low**

**MD-YIELD/NAPHTHA**          =>      **low**

**Nickel**                           **22**      **low**

**Vanadium**                      **41**      **low**

MD-YIELD/NAPHTHA		low	Iron	37	low
<b>YIELD</b>	⇒	low	<b>METALS</b>	⇒	low

Wax Content			Asphaltenes	1	low
Asphalt Content	9	low	Aromatics	4	low
YIELD		low	METALS		low
<b>WAX-ASPHALT DILUENT</b>	⇒	low	<b>HFO-ANALYSIS</b>	⇒	low

Api	light	low
Pour Point	10	high

**WAX-ASPHALT DILUENT**

<b>CRUDE ANALYSIS</b>	⇒	high
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CRUDE ANALYSIS	high
HFO-ANALYSIS	medium
DISTILLATES	medium

<b>CHEMICALS</b>	⇒	medium
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CONDITIONS	medium
PHYSICALS	medium
CHEMICALS	medium

⇒ Recommendation no. 14

This table provides the "flow plan" in which all the parameters are integrated and grouped to building blocks and functions. Classifications and assessments are using the ranges of Table 1, the diagrams in Figures 2-4, and the underlying decision trees, which are the heart of this expert system. For the list of parameters, the quantification and assigned risk ranges, the logical flow plan grouping and the decision trees the real experts are required, without those

the system will stay a dummy example only. The success of such a system depends highly on the quality of such experts.

7 FINAL ASSESSMENT:

The final recommendation is based on the three main phase assessments: 'CONDITIONS', 'PHYSICALS' and 'CHEMICALS'. In this case - recommendation no. 14, with its prescribed text is retrieved. The final report consists of several additional parts:

1. A list of comments, (labeled by \*), which point at some warning sign as a result of an important function or test result classified as risky (none in the example).
2. A recommendation, an action to be taken. This could be a time span before problems are likely to occur, advice, reference etc.
3. Any inconsistencies concerning the test results, revealed by the system (none in our case).
4. A list of all test values which have been classified by the system as high risk and medium risk.

Please note, that your information was not complete and can be improved by more data. Concluding from the above major issues and all other available data, the following can be concluded:

Recommendation no. 14

Reasonable logistical and environmental conditions plus only a slight danger from the compatibility side are leading to a basis for the storage of a medium sludge risk crude, which is acceptable at least for some time. The chemistry of the crude in hand may indicate some sludging potential but not immediately, possibly only after 3-4 years.

Please pay attention to the following values:

<u>'High Risk':</u>	<u>'Medium Risk':</u>	
Rough Climate - extrm	Sludge Stirred - un	Gravity d 15 - 0.833
Closed/Open - open	Age - 2	Pump Turbulence - some
Warming Status - none	Climate Shocks - rare	Syncrude - some
Free Water in Oil - 2500	Pipeline - short	Crude Vac. Residue - 16
Pour Point of Crude - 10	Status (Physical) - corr	Crude Light Dist. - 42
VGO Pour Point - 63	Below/Above Ground - part	Mid. Distl. Kero - 24
Mid. Distl. Wax - 89	Sludge Found - some	

## 8. DECISION JUSTIFICATION:

Explanation capability is an important feature in expert systems, as it enhances the reliability of the conclusions. The system has a few features which provide means to justify the system's decision. The expert system assessment screen could be used as a logical spreadsheet, where it is possible to type in values and to observe their impact on the evaluation process, thus performing sensitivity analysis. This feature could also be used for selection of the best storage site for a given crude, by entering on screen all the test and crude data and the details of a particular site. The system will give a prediction of the oil as if it is stored in that site. The user may ask for a list of all high risk and missing values, and for a complete reasoning sequence, listing the logical path of decisions. This tool provides a justification of the system's suggestion, and enables to pinpoint the specific apparent problem.

## 9. CONCLUSIONS:

This paper describes a demonstration expert system geared towards the prediction of crude fall-outs and sludge formation phenomena. The data, expert crude knowledge and related experience are not real, and are given only as an example. A real system could integrate knowledge of many experts in different fields of crude handling. As was mentioned earlier various entities and organizations have been collecting data and understanding of these problems. Thus, a combined effort of gathering information, experience and knowledge from appropriate experts would produce the knowledge base.

An easy user interface allows the user to update the knowledge base (test classifications, tree decisions). The system, therefore could grow and expand to incorporate new knowledge and recently acquired experience. Such a system should improve with time, and its predications and assessments become more accurate. Modularity is apparent, the top level function describing the risk profile (giving the recommendation), has three arguments, which could be developed independently without affecting the rest of the system.

The flexibility of the mentioned EQPS software, the separation between the logical shell structure and a specific knowledge base, enables to apply major mathematical algorithms and existing software tools developed in the EQPS project to the problems of crude oils.

## REFERENCES:

- [1] J. Hartman, Y. Geva, R. Fass. A Computerized Expert System for Diagnosis and Control of Microbial Contamination in Jet Fuel and Diesel Fuel Storage Systems. Proceeding of the 4th International Conference on Stability and Handling of Liquid Fuels. Orlando Florida, November, 1991.
- [2] J. Hartman, R. Fass. An Expert System for Diagnosis and Control of Microbial Effects During Fuel Storage. Update II, The British Institute of Petroleum. April, 1989.
- [3] J. Hartman, R. Fass, Y. Geva. Using a Computerized Expert System to Monitor Microbial Activity in Jet Fuel Storage Tanks. Proceeding of the Eighth Biodeterioration and Biodegradation Symp. Windsor. Canada, August 1990.
- [4] J. Hartman. The Mathematical Approach to EQPS - An Expert System for Oil Quality Prediction. Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels Rotterdam, the Netherlands, October, 1994.
- [5] J.W.J. Koenig. The EBV-Quality Prediction System (EQPS). Proceeding of the 5th International Conference on Stability and Handling of Liquid Fuels. Rotterdam, The Netherlands, October 1994.
- [6] J. Hartman, An Expert System for Strategic Oil Storage. Applications and Innovations in Expert Systems. Proceedings of Expert Systems 95, British Computer Society, Cambridge, UK, December 1995.
- [7] R Forsyth Expert Systems, Principles and Case Studies, Chapman and Hill Computing, London, 1984.
- [8] I. Bratko. Prolog Programming for Artificial Intelligence, Addison Wesley, New York, 1986.