

**PROCESS AND ECONOMICAL ASPECTS OF SYNTHETIC  
LUBRICANTS**

**Submitted for the partial fulfillment of  
Integrated B. Tech. (Applied petroleum Engineering) & MBA  
(Oil & Gas Management)**

**(Session:- August 2007-June 2012)**



**SUBMITTED TO:**

**University of Petroleum & Energy Studies, Bidholi, Dehradun**

**Under the Able guidance of: Dr. R. P. BADONI**

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**University of Petroleum & Energy Studies**

**Bidholi, Dehradun**

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(Final Project Report)

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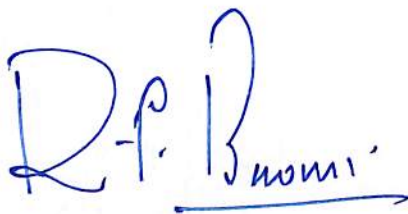
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## CERTIFICATE

This is to certify that the Major project report on “**Process and Economic Aspects of Synthetic Lubricants**” completed and submitted to the University of Petroleum & Energy Studies, Dehradun by Mr. Abhishek Kr. Singh & Mr. Digvijay Singh Yadav in partial fulfillment of the requirements for the award of degree of Inte. B.Tech. (Applied Petroleum Engineering) + MBA (O & G) is a bonafied work carried out by them under my supervision and guidance.

To the best of my knowledge and belief the work has been based on investigation made, data collected and analyzed by him and his work has not been submitted anywhere else for any other University or Institution for the award of any Degree/Diploma.



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**Integrated B. Tech. (Applied petroleum Engineering) & MBA (Oil & gas Management)**

**UNIVERSITY OF PETROLEUM & ENERGY STUDIES**

**Dehradun**

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## **ABSTRACT**

### **Scope**

As energy demand continues to rise, so does the concern over the future availability of conventional fuels. There is a growing need to find alternative fuel options, such as synthetic fuels. These fuels can be used in existing diesel engines and fuelling infrastructure and significantly reduce exhaust emissions, while diversifying energy sources and improving security of supply.

### **Objective**

To Study the characteristics of synthetic lubricants & observe their economic behavior, commercial developments and environmental impact with special consideration given to Poly ( $\alpha$ -olefin) (PAO).

### **Brief Description**

This project will cover the detailed study on following topics:

- The introduction about synthetic lubricants
- The detailed study of poly-alpha olefin
- Comparison between different synthetic lubricants
- The industrial trends and market behavior
- The commercial developments in the field of synthetic lubricants
- Cost analysis and cost estimation
- Environmental impact of synthetic lubricant use

# **CHAPTER 1**

## **POLY ALPHA OLEFIN (PAO)**

### **I. PROLOGUE:**

Saturated olefin oligomers is a class of synthetic high performance functional fluids that have been developed to meet the increasingly rigorous demands being placed on today's working fluids. The term PAO, or poly alpha olefin, is basically used to delegate such fluids, and that designation is used in this report. The term PAO was first used by gulf oil company (which was later on acquired by Chevron), but now become an accepted standard appellation for hydrocarbons manufactured by the catalytic oligomerization (which describes polymerization to low molecular weight products) of linear olefins have six or more (usually ten) carbon atoms.

Technological advances are frequently accompanied by a variety of unanticipated problems and complications. The new advances in the function and efficient operation of modern machines and engines have brought new challenges and stages relating to the satisfactory use and performance of existing present functional fluids. Among these the common challenges are:

- \*operation done under increasingly severe conditions
- \*the call for more cost effective, hence more competitive, operations
- \*the need to diminish dependence on the availability of crude oil stocks
- \*the specialized performance requirements of maturing end-use applications
- \*the requirement of accounting for the critically significant, but long-ignored, toxicological and biodegradable characteristics of the fluids being used

In the present scenario, mineral oil base stocks are being refined to produce products that are certainly superior to those offered only few years ago. But the limits to which mineral oils can be

economically refined are being overwrought. To satisfactorily concentrate on the challenge of solving the problems which are mentioned above, industry is moving to synthetic alternatives.

PAOs are basically day by day gaining rapid and swift acceptance as high performance lubricants and functional fluids because they demonstrate certain inherent, and highly desirable, perfect characteristics. Among these favorable properties are mentioned as:

An extensive operational temperature range

High-quality viscometrics (high viscosity index)

Thermal stability

Oxidative stability

Hydrolytic stability

Shear stability

Low corrosivity

Compatibility with mineral oils

Compatibility with various other materials of construction

Low toxicity

Manufacturing flexibility that allows "tailoring" products to specific end-use application requirements.

## **II. HISTORICAL DEVELOPMENT**

### **i. Technical**

Synthetic oils which consisting only of hydrocarbons molecule were first produced by the well-known Chemists Charles Friedel and James Mason Crafts in the year 1877. Standard Oil Company of Indiana attempted to commercialize synthetic hydrocarbon oil in year 1929 but was unproductive because of being deficient in demand. In year 1931 Standard Oil, in a paper published by Sullivan et al., revealed a process for the polymerization of olefins to form liquid products. These human resources employed cationic polymerization catalyst like aluminum chloride to polymerize olefin mixtures produced from the thermal cracking of wax. At about the

same time when the work at Standard Oil was being carried out, H. Zorn of I.G. Farben Industries independently revealed the same process.

The primary use of a linear alpha-olefin to manufacture oil was disclosed by Montgomery et al. in a patent issued to Gulf Oil Company in year 1951. Aluminum chloride was the one used in these experiments, as used in the earlier work with olefins from cracked wax.

The utilization of free radical indicator as alpha-olefin oligomerization catalyst was the one first patented by Garwood of Socony-Mobil in year 1960. Coordination complex catalysts, like the ethyl aluminum sesquichloride/titanium tetrachloride system, were mentioned in a patent issued to Southern et al. at Shell Research in year 1961.

The fluids manufactured by the various other catalyst systems mentioned above contained oligomers with a wide variety of molecular weights. The internal structure and composition of these fluids resulted in viscosity – temperature characteristics that provided them no particular advantage over the readily available and significantly less expensive minerals oil of the day.

In year 1968, Brennan at Mobil Oil patented a procedure for the oligomerization of alpha-olefins using a  $\text{BF}_3$  catalyst system. Aforementioned to that time,  $\text{BF}_3$  catalyst had given irreproducible results. Brennan explained that the reaction could be controlled if two streams of olefins sample were mixed in the reactor. The second stream consisted of the olefin saturated with gaseous  $\text{BF}_3$ . Of particular interest, this catalyst system formed a product consisting of mixed oligomers that is markedly peaked at the trimers.

Shubkin from the Ethyl Corporation showed that  $\text{H}_2\text{O}$ , as well as the proticco catalyst like alcohols and carboxylic acids could be used in combination with  $\text{BF}_3$  to manufacture oligomers of uniform quality. The experimental procedure employed a molar excess of  $\text{BF}_3$  in relation to the co catalyst. The excess was achieved by sparking the reaction medium with  $\text{BF}_3$  gas during the course of the reaction or by preparing the reaction under a minor pressure of  $\text{BF}_3$ . These studies explained that the results of oligomerization products exhibited pour points that were well known those predictable for such compounds, even when dimeric products were allowed to linger in the final mixture. The molecular structure of the dimer is believed to consist of a straight carbon chain consisting of a single methyl group close to the middle. The branched structures similar to those were known to exhibit relatively high pour point. Considering more pertinent to the current subject, these were the one's which are the first patents to address the potential importance of PAOs derived from  $\text{BF}_3$ , ROH catalyst system as synthetic lubricants. Shubkin et al. further showed that the unique low temperature properties could be attributed to a high degree of branching in the molecular structure.

## ii. Commercial

The commercial development of PAO fluids in the form of lubricants and high performance functional fluids began in the early 1970s, but the significant rise and growth in markets and in the variety of end-use applications did not begin until the later part of the 1980s. During this time, various other companies played significant roles with both Research & Development and market expansion as well as development efforts.

### **Amsoil Corporation**

Amsoil Corporation was it appears that the first company to market a full synthetic lubricant which was certified by American Petroleum Institute (API). However, this product, which was introduced in year 1972, was basically based on 100% diesters. It was not until late 1977 that Amsoil introduced full synthetic 10W-40 oil based on PAO/ester. Semi synthetic diesel engine oil has also been introduced by Amsoil which was a full synthetic gear oil based on PAO- based greases. In the year 1996 the firm introduced PAO/ester-based 0W-30 motor oil.

### **Mobil Oil Corporation**

Mobil Oil Corporation was the first firm which introduced a PAO-based synthetic lubricant. In the year 1973 Mobil Corporation began marketing synthetic motor oil for the purpose in automotive engines in overseas markets. Circulating oils and gear oils were the one which was added to the Mobil line in year 1974. The primary U.S. test marketing of Mobil 1 Synthesized Engine Lubricant started in the autumn of 1974. This trial was extended to eight cities in September 1975 and to all Mobil marketing areas in April 1976. Mobil 1 was initially an SAE 5W-20 product, but further it was replaced by a 5W-30 fluid based on PAO and a neopentyl polyol ester. The polyol ester enhanced additive solubility and increased seal swell.

The extension of Mobil's product distribution was done to Canada, Japan, and several other European countries in year 1977. In the year 1977 also, Mobil introduced Delvac 1, a PAO-based product which aimed at the truck fleet market. Mobil is the company which also pioneered PAO-based industrial lubricants with its line of Mobil products like SHC.

The Mobil's PAO plant which is in the United States has an expected annual capacity of 52,000 metric tons. A new plant at Notre Dame de Graven chon, France, reportedly observed that has an annual capacity of 50,000 metric tons. Mobil purchase 1-octaene, 1-decene, and 1-dodecane for the production of PAO.

With the low viscosity PAOs Mobil produces other two grades of high viscosity PAO. The annual sales for these mentioned products are supposed to be around 4000 metric tons.

## **Gulf Oil Company**

Gulf Oil Company seems to have had a real interest in synthetic hydrocarbons in the year 1940s. The Development work done at the Gulf laboratories in Hiramsville, Pennsylvania, continued smoothly in the year 1960s and 1970s. In year 1974 Gulf constructed a semi works plant with a capacity of 1125 metric tons per year. The first commercial sale from this plant was done in December 1974.

During the years 1976-1980, the company Gulf introduced an arctic super-duty 5W-20CD/SE crankcase lubricant plus arctic universal oil/transmission oil. Gulf began marketing of PAO-based gear lubricants, synthetic greases, and partial synthetic 5W-30 crankcase oil in Canada.

In December 1980 Gulf began to produce PAO in their PAO plant in Cedar Bayou, Texas, strategically positioned next to Gulf's olefin plant. The production capacity in the starting was 15,400 metric tons per day. In year 1981-1983 Gulf added various new PAO- based products to their line of synthetic fluids. These basically included Gulf Super Duty II, full synthetic 0W-30 crankcase oil, Gulf SL-H, a hydraulic fluid for low and high temperature operation, and Gulf Syngear, 75W-90 gear oil for extended life and obviously fuel economy. In addition to these fully formulated products, Gulf marketed PAO to the merchant market beneath the trade name Synfluid Synthetic Fluids. Gulf Oil Corporation was further acquired in 1984 by chevron Corporation.

## **Chevron Corporation**

Chevron marketed a single synlube-based product, before the year 1984. That product which was obtained named Chevron Sub Zero Fluid, 7.5W-20 CD/SE crankcase oil for the purpose in construction apparatus and various vehicles employed in the Alyeska Pipeline Project in Alaska. Further in June 1984 the company Chevron acquired Gulf Oil Company. The PAO manufacturing and marketing responsibilities were moved to the Oronite Division of Chevron Chemical in late 1985. Later Chevron continued to propose the PAO- based arctic oil plus Chevron Tegra PAO- based synthetic lubricants, which also contained the old Gulf Synegear and three grades of compressor oils. Other than Mobil, which selected to the market aggressively under their own name, further Chevron decided to aim basically on the merchant market. The capacity of the Chevron plant which later increased to approximately almost 24,000 metric tons. Chevron, like Amoco Corporation, but different from Mobil, is basic in the alpha-olefin raw material which is used to produce PAO fluids.

## **Amoco**

Amoco, previously Standard Oil Company (Indiana), was probably the first and the initial one of U.S. petroleum firm to explore synthetic hydrocarbon fluid. The pioneering work done by F.W. Sullivan in the early 1930s was truly challenging and appreciable. The hard work by the company led to a patent that explained the aluminum chloride catalyzed polymerization of



olefins obtained from the cracked wax. The initial attempt to commercialize a synthetic lubricant fluid in 1929, because of lack of demand was abandoned.

Amoco Oil Company began test marketing in the year 1982, a 100% PAO-based lubricant. The project was followed by the PROLOGUE of Amoco's Ultimate line of crankcase oil for both gasoline and diesel oils in April 1984. Amoco further described the product line to embrace also grease base sand gear oils. All the PAO for the Ultimate products were purchased until 1996, when both the alpha-olefin and PAO technology plants were purchased by Amoco from Albermarle Corporation. Now, Amoco currently has the technology and other resources to manufacture PAOs directly from its own ethylene.

### **Exxon Corporation**

The PROLOGUE of Esso Ultra Oil in Europe was done by Exxon in mid-1986. The lubricant was partial synthetic oil which contained PAO. The company Exxon has created small amounts of PAO in its respective alkylation facility at its chemical plant in Port Jerome, France. The very Plan to convert that plant to full-scale PAO operation appeared to have been shelved.

### **Quantum Chemical Corporation**

The Quantum Chemical Corporation is the name adopted in year 1988 by the former National Distillers and the respective Chemical Corporation. National Distillers smoothly entered the synthetic lubricants market in 1978 with the acquirer of Emery Industries, which was an important producer of ester-based synlubes.

National Distillers announced the construction of a 15,400 metric ton PAO plant at their manufacturing facility in Deer Park, Texas in the year 1980 in December. The plant basically did not come onstream until late 1983. In year 1987 National Distillers entered into a developed and marketing agreement with the one named Ethyl Corporation. The 1-decene feedstock was supplied by Ethyl.

By the year 1989, Quantum Corporation had debottlenecked the PAO plant and constructed a second, larger plant at the same site, bringing the total capacity to 77,000 metric tons. The Quantum Corporation sold their PAO business and manufacturing site to Ethyl Corporation in the year 1990. In 1994 Ethyl spun off Albermarle Corporation. The PAO business and production location became a part of Albermarle Corporation, but, was sold to Amoco in March 1996.

### **Castrol Limited**

Castrol, which was originally the Burmah Oil Public Limited Company, and then Burmah-Castrol, has historically been a trend setter in the field of automotive lubricant marketing, In 1981 Castrol purchased the one named Bray Oil Company, a small manufacturer of synthetic lubricants based in California .At the same time the Bray Oil Company had been toll-producing

PAO for Ethyl Corporation. Although Castrol maintained a tough attention in marketing synthetic lubricants, they basically selected and decided to close the PAO plant and purchase their PAO requirements.

Castrol Limited was precisely an early dealer of synthetic automotive lubricants in Europe. The PROLOGUE as a full line of synthetic and compressor oils and semi synthetic gear lubes as well as better and higher performance jet turbine oils, military hydraulic fluids and jet lube products. They PROLOGUE of Syntron X-a 5W-50 PAO-based automotive synlube-into the United Kingdom was done in the year 1988, and a new line of PAO-based automotive products as well, under the deal names Syntroque and Transmax, was introduced into the United States in 1991. Further Castrol introduced a 5W-50, Syntec PCMO in year 1993 just followed by a 10W-30 oil. The PROLOGUE of Synthetic Blend also, becomes a synthetic part, in the late years of 1995.

### **Uniroyal Chemical Company**

In view of the fact that 1980, Uniroyal has manufactured high viscosity PAOs (kinematic viscosities at 100°C of 40 and 100 CST) in a small plant at Elmira, Ontario. Uniroyal and Mobil are precisely the only producers of these grades of PAO in the world. Total production capacity of them is about 2000 metric tons per year.

### **Neste Chemical**

Neste Chemical has a PAO plant which is in Beringen, and Belgium. The facility came on-stream in year 1991 and was predicted to have a functional capacity of 28,000 metric tons. Current predicted production now is estimated to be 35,000 tons per year.

### **Texaco**

Texaco has maintained research on PAOs and holds various patents but do not contains commercial production. But as a matter of fact they do, however, market PAO- based lubricants underneath the trade name Havoline.

### **Shell Chemical**

Shell Chemical has done widespread research on PAOs but they did not begun commercial manufacturing. Shell, along with the two worthy company Chevron and Amoco, is basic in the alpha-olefin raw material.

### **Idemitsu Petrochemicals**

PAOs are now not currently manufactured in Japan. However, Idemitsu Petrochemicals raised their interest in the plant construction many years ago. To date, they have not announced the plans to build a PAO plant on their own or with any other company.

## Sasol

In South Africa Sasol the production is 1.4 million metric tons/year of mixed alpha-olefin from the process in which conversion is done from coal to hydrocarbons via Fischer-Tropsch chemistry. Sasol is on the other hand considering plans to manufacture PAOs and oxo alcohols in the future.

Sasol has announced their plans recently to almost double its alpha-olefins capacity at its coal to synthetic fluids facility in South Africa. By fourth quarter of 1997, Sasol will be in a position having a capacity of 110,000 metric ton/year of hexane with further expansion planned in 1998-1999, in which pentane capacity is also expected to be included.

Sasol is expected to spend over \$50 million to construct a 50,000 metric ton/year 1-octene unit at the facility. The expectation for this unit is to be on-stream by 1999.

### III. CHEMISTRY

PAOs are manufactured by a two-step reaction sequence from linear alpha-olefins, which are basically derived from ethylene. The first step for this is synthetic of a mixture of oligomers, which are polymers of relatively low molecular weight. This is shown as:

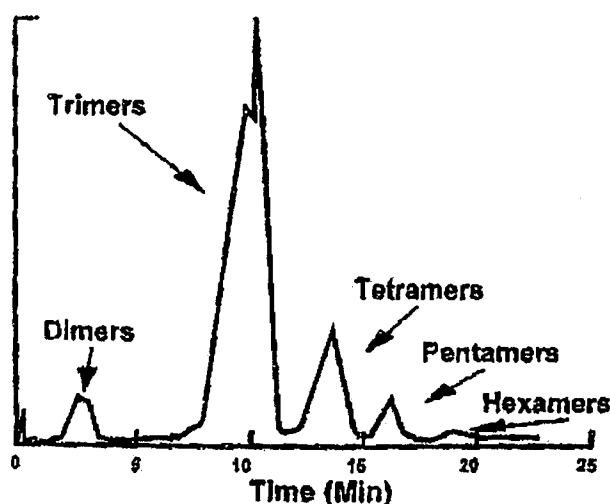
Alpha-olefin---dimer + trimer + tetramer + pentamer, etc.

For the manufacture of low viscosity PAOs (2-10 cst), the catalyst used for the oligomerization reaction is usually taken boron trifluoride ( $\text{BF}_3$ ). (PAOs are commonly classified on the basis of their approximate kinematic viscosity which is at 100 °C – this convention is used throughout this article.) The  $\text{BF}_3$  catalyst taken here is used in conjunction with a protic co-catalyst like water, an alcohol, or a weak carboxylic acid. It is necessary that the catalyst  $\text{BF}_3$ , which is a gas, be maintained in a molar excess relative to the protic co-catalyst. Although this stoichiometry may be proficient by sparging the prospective reaction mixture with a stream of  $\text{BF}_3$ , it becomes more practical, on a commercial basis, to conduct the reaction beneath a slight  $\text{BF}_3$  pressure (10-50psig). For the convenience, a general description for the catalyst stream is  $\text{BF}_3 \cdot \text{ROH}$ , where ROH present here shows any protic species likewise those mentioned above, and the presence of excess  $\text{BF}_3$  is understood.

The  $\text{BF}_3$  .ROH catalyst system is very unique mainly because of two reasons. The first one, this catalyst combination gives an oligomer distribution that is markedly peaked at trimer. Figure 1, which shows a gas chromatography (GC) trace indicating and explaining the oligomer distribution of a distinctive reaction product derived from 1- decene using a  $\text{BF}_3$  .n-  $\text{C}_4\text{H}_9\text{OH}$  catalyst combination at a temperature used for the reaction which is  $30^\circ\text{C}$ . The chromatogram shows that only a relatively less amount of dimer is produced. The bulk of the product found is the trimer, found with much smaller amounts of higher oligomers present.

The second unique feature of the very same  $\text{BF}_3$ .ROH catalyst system explains that it manufactures products that are obtained have exceptionally good low temperature properties. The extremely low pour point values mystified the early workers in the field until it was found that the resulting oligomers demonstrates a greater degree of skeletal branching than would be predicted by a conventional cationic polymerization system.

The reason behind  $\text{BF}_3$  catalysis cause excess skeletal branching during the process of oligomerization is unclear. The first researcher to discover the phenomenon proposed a mechanism which explained involving a skeletal rearrangement of the dimer. Further a later paper projected that the monomer undergoes rearrangement. A third paper projected that the excess branching arises because of the positional isomerization of the double bond in the monomer prior to oligomerization process. In fact, the higher number of isomers that are produced cannot be described by any of the single mechanism, and the role of  $\text{BF}_3$ . ROH in promoting the necessary rearrangements remains unsolved.



**Figure 1 – Gas Chromatography of typical oligomer**

Even though the method of the  $\text{BF}_3$ . ROH-catalyzed oligomerization remains to be fully elucidated, researchers have found and learned how to advantageously control the composition

of the needed final PAO product to allow the tailoring of the oligomer distribution to fit the necessities of specialized end-use application. This customizing is done by alteration of the reaction variables, which consists of:

Chain length of olefin raw material

Temperature

Olefin feed rate

Pressure

Co-catalyst feed rate

Catalyst concentration

Co-catalyst type and concentration

Time

Reaction quench and recovery procedures

Hydrogenation catalyst and conditions

Distillation

In addition to controlling the relative sharing of the oligomers by treatment of the reaction parameters, the PAO producer can make major modifications in the obtained product properties by selection of starting olefin. Today, the commercial PAO marketplace is dominated by decene-derived materials because these products have the broadest variety of properties, but a knowledgeable producer has the option of selecting other initial olefins to satisfy better the requirements for a particular end-use function application. Taking an example, PAO based on C<sub>12</sub> olefin is manufactured commercially by chevron and Mobil. Mobil also prepares PAO materials which contain oligomers based on 1-octene, and 1-decene, and 1-dodecene mixtures.

The crude reactions manufactured is quenched with water or caustic, permitted to settle, and then washed again with additional water to remove all traces of the BF<sub>3</sub> catalyst. Gaseous BF<sub>3</sub> can be improved and recovered by concentrating the wash water and treating the solution with concentrated sulfuric acid.

A second step in the process of manufacturing entails hydrogenation of the unsaturated oligomer. The hydrogenation reaction may be done before or after distillation. Distillation is required to eliminate any other un-reacted monomer, to separate the dimer, which is found and marketed as a 2.0cst product, and in some cases to produce at the same time a lighter and a heavier grade of PAO.

The hydrogenation is characteristically performed over a supported metal catalyst like nickel/kieselguhr or palladium/alumina. Hydrogenation is needed to obtain the final product enhanced chemical inertness and added oxidative stability. The expression poly (alpha olefin) is used even though the fluid is saturated in a consequent chemical hydrogenation.

It is normally impossible to produce the higher viscosity PAO products (40 and 100 cst) by means of the  $\text{BF}_3 \cdot \text{ROH}$  technology. However, various other catalyst systems are known that can produce the respective products which are desired. One class of catalyst employs alkyl aluminum compounds in combination with  $\text{TiCl}_4$  or alkyl halides. The latter system is favored by Uniroyal, which use ethyl aluminum sesquichloride with the alkyl chloride.

It has also been found in a Mobil Oil European patent application that the high viscosity PAOs may be manufactured by dimerizing lower oligomers with peroxide. The patent explains the use of stoichiometric quantities of di-tert-butyl peroxide, which almost certainly would not be economically reasonable. On the other hand, a system that employs hydrogen peroxide in a straight line or the regeneration of an active transitional or intermediate might be commercially attractive. Mobil has also found a large number of patents which describes the use of supported chromium catalyst. The system basically employed by Mobil for commercial production has not been disclosed, but it is thought to employ an aluminum chloride catalyst.

#### **IV. PROPERTIES**

The physical and chemical properties of PAO fluids make them eye-catching for a diversity of application requiring a broader temperature operating range than can normally be obtained by petroleum based products (mineral oils). An excellent evaluation of poly (alpha-olefin)-based fluids as high performance lubricants has recently been published which describes the properties of commercially available PAOs.

##### **A. Physical Properties**

###### **1. Commercial PAOs**

Table 1 explains the typical physical properties of the five grades of commercial low viscosity PAOs accessible today. These products are all developed using 1-decene as the initial material, and the final properties are obtained by control of the reaction parameters and (which depends on the manufacturer) selective distillation of the light oligomers.

Table 1 explains that all commercial grades of low viscosity PAOs have comparatively high viscosity indexes (VIs) of around 135. The viscosity of a high VI fluid transforms less dramatically with changes in temperature as compared to the viscosity changes found for a low VI fluid. A realistic consequence of this property is that PAOs do not need viscosity index improvers (VIIs) in different applications. The presence of a VII is often objectionable because many of these agents have a propensity to be unstable toward shear. Once the VII starts to break down, the fully formulated fluid found “out of grade” (i.e., fails to hold on to the original viscosity grade).

Various other different important physical properties of commercial PAOs are mentioned on Table 1. All the products have extremely low pour points and also very low viscosities at low temperatures. These properties found make PAOs very attractive in the cold-climate applications for which they were initially used. At the other end of the spectrum, all but the 2.0 cst products have low volatilities, as established by the low percent loss of material at 250 °C in the standard NOACK volatility test. Low volatility is significant in high temperature operations to trim down the need for “topping up” and to avoid a fluid from losing its lighter components and finally becoming too viscous at low or ambient temperature. Low volatility is also important since it relates to flash and fire points.

The typical physical properties of commercial high viscosity PAO fluids are mentioned in Table 2. The two grades accessible today on the market are the 40 and 100 cst fluids. As with the low viscosity PAOs, these fluids have a very wide temperature operating range.

**Table 1: Physical Properties of Commercial Low Viscosity PAOs**

Parameter	Test method	PAO 2	PAO 4	PAO 6	PAO 8	PAO 10
Kinematic viscosity, cst						
At 100° C	ASTM D-445	1.80	3.84	5.98	7.74	9.87
At 40° C	ASTM D-445	5.54	16.68	30.89	46.30	64.50
At -40° C	ASTM D-445	306	2390	7830	18,200	34,600
Viscosity index		--	124	143	136	137
Pour point, °C	ASTM D-97	-63	-72	-64	-57	-53
Flash point, °C	ASTM D-92	165	213	235	258	270
NOACK, % LOSS	DIN 51581	99.5	11.8	6.1	3.1	1.8

Viscosity at ° C.

**Table 2: Physical Properties of Commercial High Viscosity PAOs**

Parameter	Test method	PAO 40	PAO 100
Kinematic viscosity, cst			
At 100 °C	ASTM D-445	40 – 42	103 – 110
At 40 °C	AASTM D-445	399 – 423	1260 – 1390
At -18 °C	ASTM D-445	39,000 – 41,000	176,000 – 203,000
Pour point, oC	ASTM D-97	-36 to -45	-21 to -27
Flash point, ° C	ASTM D-92	275 -280	280 – 290
NOACK	DIN 51581	0.8 – 1.4	0.6 – 1.1

Viscosity at 250 ° C.

## 2. Comparison to Mineral Oils

The excellent physical properties of the commercial PAO fluids are most voluntarily obvious when they are evaluated directly with the petroleum –based mineral oil. The fairest evaluation is to look at fluids with nearly similar kinematic viscosities at 100 ° C. The differences in both high and low temperature properties can be evaluated.

Table 3 evaluates the physical properties of a commercial 4.0 cst PAO with those of two 100N (neutral) mineral oils, and 100NLP (low pour) mineral oil, and a hydrotreated VHVI (very high viscosity index) mineral oil. The PAO describes markedly better properties at both high and low temperatures. At high temperature it is found that, the PAO has lower volatility and a higher flash point. A relatively high flash point is, of course, generally important for reasons of safety. At the low end of the temperature scale the difference are equally remarkable. The pour point of the PAO is -72° C, while the three 100N mineral oils and the HVI oils are -15, -12, -15, -27° C, -18 and -38, respectively.

**Table 3: 4.0 cst Fluids**

Parameter	Test method	PAO	100N	100N	100NLP	VHVI	VHVI	VHVI
Base oil group		IV	I	I	I	III	III	III
Kinematic viscosity, cst								
At 100 °C	ASTM D-445	3.84	3.81	4.06	4.02	3.75	4.2	3.98
At 40 °C	ASTM D-445	16.7	18.6	20.2	20.1	16.2	--	16.61
At -40 °C	ASTM	2390	Solid	Solid	Solid	Solid	NR	NR



	D-445							
Viscosity index		124	89	98	94	121	127	141
Pour point, °C	ASTM D-97	-72	-15	-12	-15	-27	-18	-38
Flash point, °C	ASTM D-92	213	200	212	197	206	210	225
NOACK, % loss	DIN 51581	11.8	37.2	30.0	29.5	22.2	13	13.3

Table 4 compares and evaluates a commercial 6.0 cst PAO with a 160HT (hydro treated) mineral oil, a 240N oil, a 200SN (solvent neutral) mineral oil, and VHVI mineral oils which are currently measured to be the best of the mineral oils on the market. The wider temperature range of the PAO is again evident. Table 5 makes identical comparison for 8.0 cst fluids.

The capacity of PAO products to do better than petroleum-based products of identical viscosity at both the ends of the temperature spectrum becomes easily understandable if one evaluates the gas chromatography traces. Figure 2 explains chromatograms run under similar conditions of a 4.0 cst HVI oil and a 4.0 cst PAO. The PAO product is fundamentally decenotrimer with a small amount of tetramer present. The fine arrangement of the trimer peak is recognized to the presence of a diversity of trimer isomers (same molecular weight, but different arrangement). The HVI oil, on the other hand, has an extensive spectrum of different molecular weight obtained products. The oil possesses low molecular weight materials that unfavorably affect the flash point and volatility individuality. It has also high molecular weight components that raise the low temperature viscosity and linear paraffins which increase the pour point.

Figure 3 shows the GC traces of a very high quality 6.0 cst VHVI fluid with a PAO of identical viscosity. The PAO has a precise chemical composition consisting of decenotrimer, tetramer, pentamer, and a small amount of hexamer. The VHVI fluid, like the HVI fluid in the earlier example, contains a wide range of components that degrade performance at both ends of the temperature scale.

**Table 4: 6.0 cst Fluid**

Parameter	Test method	PAO	160HT	240N	200SN	VHVI	VHVI
Base oil group <sup>a</sup>		IV	II	I	I	III	III
Kinematic viscosity, cst							
At 100 °C	ASTM D-445	5.98	5.77	6.98	6.31	5.14	5.9

At 40 °C	ASTM D-445	30.9	33.1	47.4	40.8	24.1	NR <sup>b</sup>
At -40 °C	ASTM D-445	7830	Solid	Solid	Solid	Solid	--
Viscosity index		143	116	103	102	149	127
Pour point, °C	ASTM D-97	-64	-15	-12	-6	-15	-12
Flash point, °C	ASTM D-92	235	220	235	212	230	225
NOACK, % loss <sup>c</sup>	DIN 51581	6.1	16.6	10.3	18.8	8.8	6

<sup>a</sup> Base stock classification as defined by SAE classification J357

<sup>b</sup> Not reported

<sup>c</sup> Volatility at 250 °C

**Table 5: 8.0 cst fluids**

Parameter	Test method	PAO	325SN	325N
Base oil group <sup>a</sup>		IV	I	I
Kinematic viscosity, cst				
At 100 °C	ASTM D-445	7.74	8.30	8.20
At 40 °C	ASTM D-445	46.3	63.7	58.0
At -40 °C	ASTM D-445	18.200	Solid	Solid
Viscosity index		136	99	110
Pour point, °C	ASTM D-97	-57	-12	-12
Flash point, °C	ASTM D-92	258	236	250
NOACK, % loss <sup>b</sup>	DIN51581	3.1	7.2	5.1

<sup>a</sup> Base stock classification as defined by SAE classification J357.

<sup>b</sup> Volatility at 250 °C

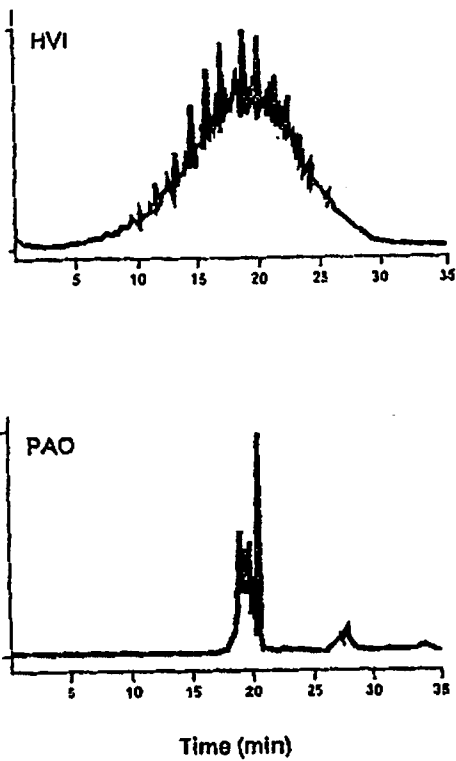


Figure 2 – Gas Chromatography traces of two 4.0 cst Fluids

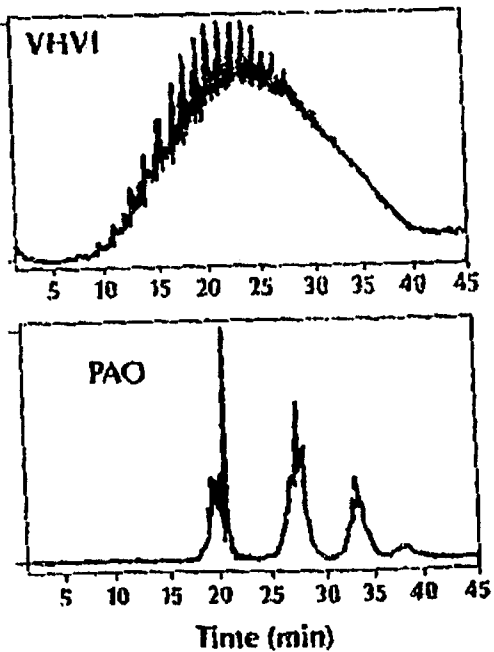
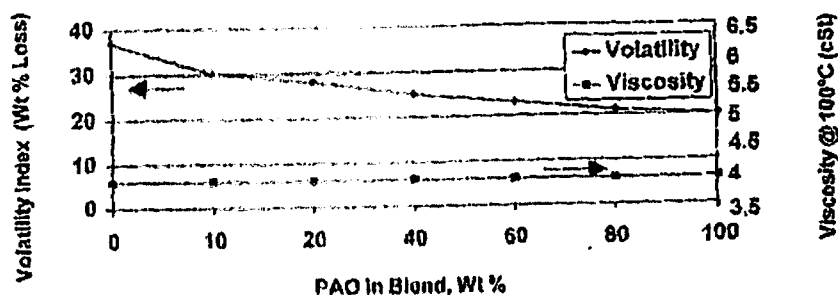


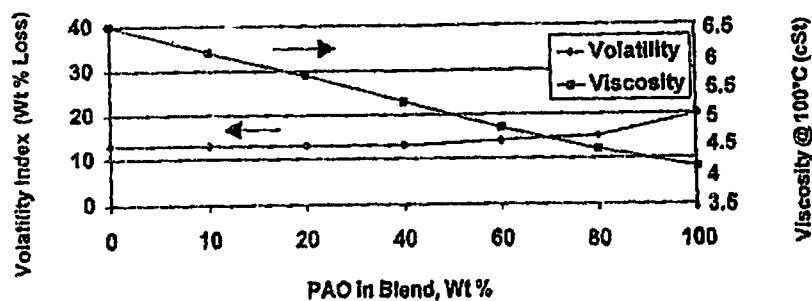
Figure 3 – Gas chromatography traces of two 6.0 cst fluids

### 3. Properties of Blends

The excellent grouping of low and high temperature physical characteristics of PAOs, combined with their total miscibility with mineral oils, shows them attractive participants for blending with certain base stocks to enhance the base stock quality and fetch it into specification for a particular and basic application. This practice has certainly become widespread (but little publicized) as refiners move quickly to meet the newer and more stringent API classification requirements.



**Figure 4** – Effect of blending 4.0 cst PAO with 100N mineral oil. Using an in house test designed to give approximate correlation to ASTM D-972. (Weight percentage loss after 2.0 hours at 204°C under flow of N<sub>2</sub>)



**Figure 5** – Effect of blending 4.0 cst PAO with 200N mineral oil. Using an in house test designed to give approximate correlation to ASTM D-972. (Weight percentage loss after 2.0 hours at 204°C under flow of N<sub>2</sub>)

Figure 4 explains the effect on volatility and viscosity in the lead blending 4.0 cst PAO with a light (100N) mineral oil. The “Volatility Index” described in this and the following figure is produced from an “in-house” test. A distinct quantity of the test example is placed in a small container or planchet, which is positioned in an oven for 2.0 hours 204° C. A constant flow of

nitrogen is maintained over the illustration (sample) throughout the test. The values are not the similar as obtained in the standard ASTM D-972 or NOACK tests, but they have been shown to associate well on a comparative basis. Small amounts of PAO have dramatic effects in dropping the volatility of the mineral oil, while having basically no effect on effect of blending the same 4.0 cst PAO with a heavy (200N) mineral oil. In this case, small quantities of the PAO have a huge effect in dropping the viscosity of the mineral oil without raising the volatility.

## **B. Chemical Properties**

In adding together to the physical properties, the chemical properties of a functional fluid must be measured. The most important chemical properties necessities are that the fluid be thermally stable and chemically inert. Under normal procedure conditions a working fluid must neither thermally corrupt nor react with the atmosphere, the materials of construction, seals, paints, varnishes, performance-enhancing additives, other fluids with which it is intentionally contacted, or unintentional contaminants.

### **1. Thermal Stability**

Many of the procedures calling for a functional fluid are done at elevated temperatures. For this reasons it is necessary that the fluid employed not be corrupted under the operating conditions. The choice of a suitable bench test, however, is frequently difficult. It is important that the test differentiate between thermal and oxidative degradation while simulating real-world working conditions. It is also important that the test distinguish between thermal degradation and volatility. Some evaluations based on even aging or thermo gravimetric analysis (TGA) have led to incorrect conclusions because the loss in sample weight and/or increase in viscosity could be accredited to volatization of the lighter components to a certain extent than chemical degradation.

One test usually employed that stops the danger of misinterpreting volatility for thermal instability is the panel coker thermal stability test. In the test, an aluminum panel heated to 310 °C is alternately marked by the test oil for 6 minutes and parched for 1.5 minutes. At the end of the test, the panels are marked and rated for sanitation. A completely clean panel shows a rating of 10. Table 6 describes and summarizes the results of one and several synthetic base stocks for crankcase applications. Under these sever conditions; the mineral oil panel was enclosed with deposits, indicating a lack of thermal stability. An alkylated aromatic also performed poorly. By comparison, the performance of both a PAO of comparable viscosity and a dibasic ester was

good. The best performance was attained using a mixture of PAO and a polyol ester. Dibasic and polyol esters are commonly used in conjunction with PAO in crankcase formulations.

**Table 6: Thermal Stability Panel**

Coker Test

Base fluid	Cleanliness
4.0 cst Mineral oil	0
4.0 cst PAO	8.0
5.0 cst Alkylated aromatic	2.0
5.4 cst Dibasic ester	8.0
4.0 cst PAO polyol ester	9.5

Test conditions

Panel temperature, 310 °C  
 Sump temperature, 121 °C  
 Operation, 6 min splash/1.5 min bake  
 Rating system, 10 = clean

The thermal stability of PAOs was also searched regarding use in aviation lubricants. In this assessment, thermal stability was found by heating the fluid at 370 °C under a nitrogen atmosphere for 6.0 hours in a preserved autoclave. Thermal degradation was assessed by the change in viscosity and by gas chromatographic analysis. The test explains that the thermal stability of PAO products can be marked as follows:

**Dimer > Trimer > Tetramer**

These observations are steady with the molecular structure of the oligomers. The least thermally established parts of the molecule are the tertiary carbon positions (i.e., the points where there are branches in the carbon chains). The higher oligomers have more branches and thus are more subject to thermal degradation.

**Table 7: Thermal Stability as a Function of Oligomer**

	Viscosity loss (cst)			Oligomer (%)			
	At 250 °C	At 300 °C	At 371 °C	Dimer	Trimer	Tetramer	Pentamer
2 cst	-0.2	-1.1	-49.9	90	9.0	--	--
4 cst	-0.9	-5.3	-79.7	0.6	84.4	14.5	0.5
6 cst	-2.4	-16.9	-88.4	0.1	33.9	43.5	17.4
8 cst	-4.0	-22.4	-92.3	--	6.0	55.7	27.2

10 cst	-4.4	-22.9	-94.3	--	1.1	42.5	32.3
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Thermal stability as measured by Federal Test Method 791B (modified) shows that the thermal stability of PAOs is related to the amount of dimer, trimer, tetramer, and pentamer present.

## 2. Hydrolytic Stability

The inertness of a determined fluid to reaction with water is important for a range of reasons. Hydrolytic degradation of different substances leads to acidic products which, finally, promote corrosion. Hydrolysis may also significantly change the physical and chemical properties of a base fluid, thus making it unsuitable for the planned use. Systems in which the working fluid may irregularly contact water or be uncovered to high levels of moisture are particularly and highly at risk. Also at risk are systems that function at low temperature or cycle between low and high temperatures.

The excellent hydrolytic stability of PAO fluids was marked as a result of tests conducted to achieve a replacement for 2-ethylbutyl silicate ester as a coolant/dielectric fluid for aircraft used by the U.S. military in aircraft radar system. This test process required treating the fluid with 0.1 % water (or 0.1 % seawater) and maintaining the fluid at 170 ° F (250 ° F) for up to 200 hours. Samples were inhibited at 20-hour intervals, and the flash points were calculated by the method named closed-cup. A decrease in flash point was interpreted as being investigative of hydrolytic breakdown to form products of lower molecular weight. The PAO demonstrated no decrease in flash point under any of those test conditions done, while the 2-ethylbutyl silicate ester showed noticeable decreases. Figure 6 explains the results for tests at 250 ° F.

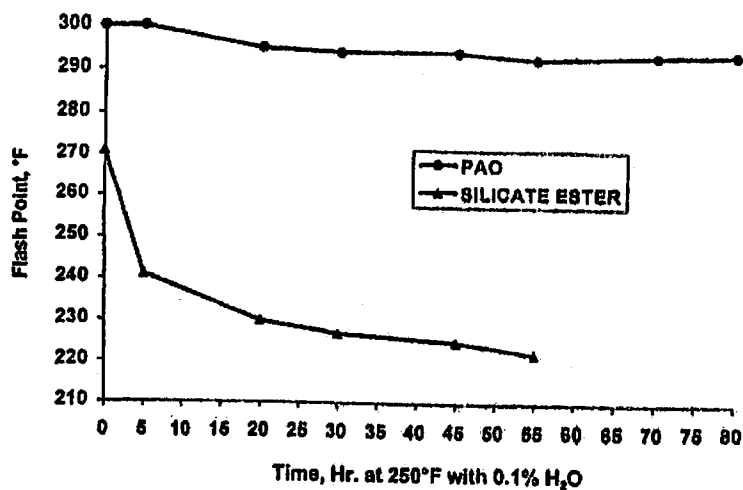


Figure 6 – Hydrolytic Stability

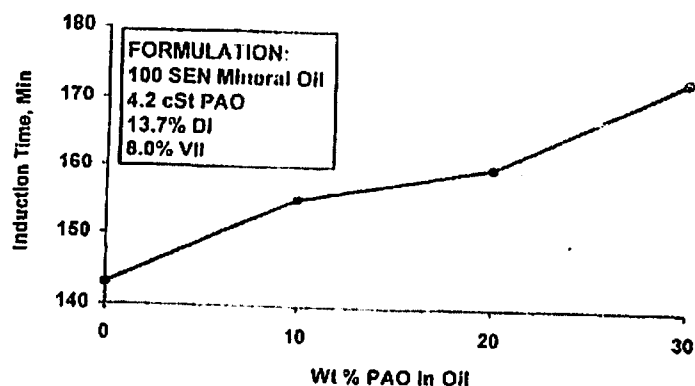
### 3. Oxidative Stability

An increased level of oxidative stability is necessary to the performance of a functional fluid. In many of the applications the fluid is required to perform at increased/raised temperature and in contact with air. The results for attempts to estimate fluids for oxidative stability, however, are a lot confusing. The results are dependent very much on the test methodology. Tests involving these thin films tend to give several results than tests using bulk fluids. Not only the presence or absence of metals that catalyze oxidation very important, but also different metals interact differently with different fluids. In addition to that, oxidative stability may be improved by the use of antioxidants, but different fluids act in response differently to different antioxidants.

One set of experiments that attempted to make a distinction between PAOs and mineral oils entailed using (degree of difference) differential scanning calorimeter (DSC). In this test, the fluid is heated in a container (pan) at a controlled stable rate, and the temperature at which an onset of oxidation takes place is obtained by the accompanying exotherm. All the commercial PAO products (with the exception of 2.0 cst fluids) were checked. The onset temperature for these six viscosity grades was found fell in the very narrow range of 187.3-191.6 °C. Two 6.0 cst mineral oils showed values of 189.2 and 206.6 °C, respectively. Quite a unlike result were found for a laboratory oxidation test in which the fluid was heated at 163 °C for 40 hours in the presence of steel, aluminum, copper and lead coupons. In this test a 4.0 cst mineral oil exhibited a 560% viscosity rise and a light sludge appearance, while a 4.0 cst PAO showed only a 211% viscosity increase with no sludge. These results appeared to indicate better performance for the PAO, but the loss of weight by the lead coupon in the PAO was found 2.8 times that of the coupon in the mineral oil. The same paper shows better performance for mineral oils in a rotary bomb test that basically measures the time for a specific pressure drop, but better performance for PAOs in beaker oxidation tests where the increase in viscosity is calculated.

The malfunction of unstabilized PAO to do better than unstabilized mineral oil in oxidative stability tests has been cautiously attributed to the presence of natural antioxidants in the afterward. The lack of inhibitors in the pure PAO is then shown as the rational for the greater receptiveness of the PAOs to the addition of small quantities of antioxidants. An interesting and somewhat identical rationale has been provided for the usually good responsiveness of PAOs to the addition of anti-wear and various other performance additives. These researchers from the All-Union Scientific Institute of Oil Refining in Moscow wrap up that the efficiency of small concentrations of additives in PAO oils is associated to the fast adsorption of the additives on the metal surface, because there is small interference of the procedure in transportation from the bulk oil to the tribo-surface. The low level of interference is a reason of weak cohesive forces between the additive molecules and the PAO substrate.





**Figure 7 – Thin film oxygen uptake test for fully formulated oils.**

The arguments mentioned above are supported by results obtained from oxidative stability testing of fully formulated part-synthetic engine oils. A thin film oxygen uptake test (TFOUT) was used for these studies. This test is basically a modified rotary bomb oxidation method in which the bomb is charged or fed with sample, a small amount of water, a fuel catalyst, and a metal catalyst. The bomb is afterwards pressurized with pure oxygen, positioned in a bath at 160 ° C, and moved axially at 100 rpm at a 30° angle from the horizontal. The time from the beginning of the test until a drop in pressure is noted and is defined as the oxidation induction time of the oil. The test oil each contained 13.7 % of a detergent-inhibitor package (DI) and 8.0% of a viscosity index improver (VII). The base stock consisted of 100 SN mineral oil which is blended with a 4.2 cst PAO. Figure 7, shows that as the percentage of PAO in the sample were raised from 0% to 30%, for the onset the induction time of oxidation increased from 143 minutes to 173 minutes. Two other papers of interest regarding the oxidative stability of PAOs are also referenced.

## V. APPLICATIONS AND PERFORMANCE CHARACTERISTICS

The use of PAO –based functional fluids is growing quickly. Conventional applications, like automotive crankcase, are being spurred on by tighter condition and an increasing demand for higher and better performance. Non-conventional applications are also found that beginning to grow rapidly, especially where specific properties of PAO fluids given them exacting advantages in performance, cost effectiveness, or environmental acceptability and strength. The confidence of original equipment manufacturers (OEMs) in PAO-based synthetic formulations is established

by factory-fill crankcase use in expensive high performance vehicles such as the Chevrolet Corvette and the Dodge Viper.

Porsche has also recently announced the authorization of PAO –based full synthetic SAE 5W-40 and SAE 10W-40 Mobil 1 for the factory fills for all Porsche passenger cars. Audi uses PAO-based full synthetic (0W-30) in superior automobiles. BMW factory-fill full synthetic gear oils are used for rear axle and manual transmission in passenger cars and also Ford-Europe has a factory-fill partial synthetic for its very manual transmissions.

### **A. Overview of Application Areas**

Both established and emerging application felids for PAOs are shown below. The list of applications has increased to such an extent in the last few years that a comprehensive evaluation of the PAO performance attributes establish advantageous in each and every application would require bigger and larger space than is present here. Instead, where possible, a reference is marked so that the reader may submit to published information and data in the precise area of interest. Describing this section, some performance data for areas of the broadest interest are explained.

**Table 8:**

Engine crankcase	Compressor oils
Gear oils	Dielectric fluids
Shock absorbers	Textiles
Automatic transmission fluids	Polymers
Metalworking fluids	Heat transfer media
Hydraulic fluids	Off-shore drilling muds
Greases	Turbine oils
Mining and conveyer	Space application
Brake fluids	Cosmetics and personal care products
Pumps	Gels for coating optical fibers

### **B. Performance Testing for Automotive Applications**

While the physical properties are obviously important in selecting a fluid for a specific application, it is necessary that the fluid is subjected to performance testing below conditions that simulate the range to which the final product obtained will be stressed. But, as mentioned above, the list of applications for PAOs is now very large that it precludes a comprehensive argument of performance testing for all applications. Because the requirements for the extensive variety of automotive applications include much of the broader spectrum of application, this particular

section will focus on some of the tests particularly designed and conducted by the automotive industry.

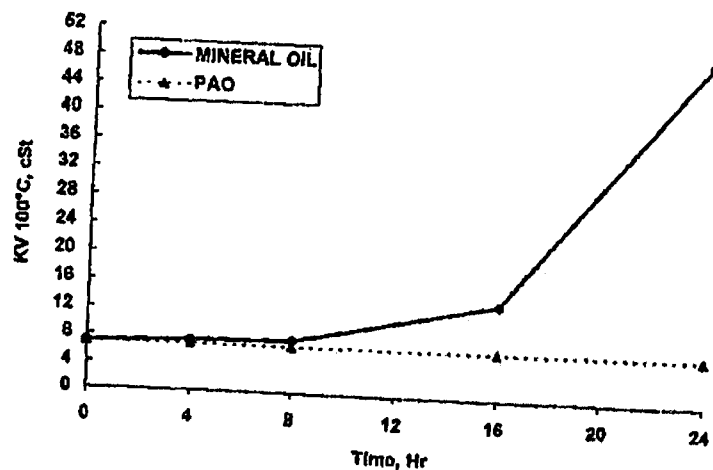
An excellent description of the automotive testing conducted in the 1970s and early 1980s observed in a collection of 26 papers which was published in one volume by the Society of Automotive Engineers (SAE). In SAE published article, the editors summarize the "eight superior performance characteristics of synthetic engine oils." Their conclusions were based on a compilation of data in the several papers. The eight particular features which they identify are mentioned:

- **Improved engine cleanliness:** This feature is based on a test using four taxicabs employing SAE 5W-20 PAO-based oil. Oil changes at 12,000 miles for the first 60,000 miles were followed by a 40,000 "no drain" phase.
- **Improved fuel economy:** The outcome of 10 different test programs involving a total of 182 vehicles described a weighted average fuel savings of 4.2%.
- **Improved oil economy:** In 10 different tests on oil consumption it was found that, the percent improvement in miles per quart varied from 0% (for a military arctic lubricant) to 156%. The average improvement noticed was 55.9%.
- **Excellent cold starting:** Automobiles with 400 CID V-8 engines could be initialized at -39°F when the crankcase enclosed SAE 5W-20 PAO- based synthetic oil. With a mineral oil of the similar viscosity grade the lowest engine starting temperature found was -29°F.
- **Excellent low temperature fluidity:** For the two oils mentioned in the respective item 4, the PAO-based oil showed a pour point of -65 ° F, whereas the mineral oil contained a pour point of -37 ° F.
- **Outstanding performances in extended oil drain field service:** This conclusion mentioned is based on 100,000-miles tests using parkway police cruisers, which are normally done at speeds ranging from 55 to 100 mph. The vehicles basically used a PAO-based SAE 5W-20 "SE-CC" oil. Oil filter changes were performed every 25,000 miles. The baseline consisted of a sequence of tests carried out in similar vehicles operated on SAE 10W-40 "SE" mineral oil with oil and filter changes for every 5000 miles.
- **High temperature oxidation resistance:** Viscosity rise was observed in a 2-L Renault after 64 hours of procedure with an oil sump temperature of 302 ° F. The synthetic oil showed a 10% rise in viscosity and the mineral oil showed a 135% rise. Both the samples were noted SAE 10W-50 oils.
- **Outstanding single and double length SAE-ASTM-API "SE" performance tests:** The results of all these tests are found very bright and appreciable. The PAO- based synthetic oils met or exceeded the complete requirement.

More recent data explained that PAO-based fluids continue to give superior performance for the increasingly sophisticated cars which are now being made. Today's automobile's share a tendency to have smaller, more demanding engines. Increased stress on aerodynamics means less cooling under the hood, resulting in higher operating temperatures in cooperation with the engine and the transmission. In addition to the capability of PAO to meet this challenge with outstanding thermal and oxidative stability, PAOs offer other advantage over mineral oils under these rigorous operating conditions. Both the thermal conductivity and the heat capability of PAO fluids are found almost 10% higher than the values for the equivalent mineral oils. The final result is that PAO-lubricated equipment tends to run cooler. Fully synthetic automotive lubricants for engine oils, automotive transmission fluids, gear oils, and grease applications offer improved shield of hardware.

**Table 9 – Hot oil oxidation test (200°C); Manual transmission and rear Axle Oils**

Time (h)	Kinematic viscosity at 100°C (cst)	
	PAO	Mineral oil
0	10.00	10.50
4	10.45	12.60
8	11.54	12.90
16	11.92	51.24
24	12.10	Too viscous to measure



**Figure 8 – Hot oil oxidation test (automatic transmission, 200°C)**

### **C. Performance Testing for Industrial Application**

Poly ( $\alpha$ -olefins) have served as the lubricant of selection in industrial application and use for over a decade. Some of these also consist of sealing fluids and lubricant for pumps handling polystyrene process liquid at 232.2 °C (450 °F) in nitrogen atmosphere. PAOs have also been used as a substitution for polyolester as a high temperature bearing and gear lubricant in blowers which were used as a steam booster compressor. Rotary and reciprocating mechanical vacuum pumps are lubricated applying ISO 46 PAO formulations. The chemical inertness of PAOs has been established in chemical applications. PAOs give satisfactory performance as:

Lubricants for huge conveyor chains with exposure to sulfuric acid vapors

Lubricants used for reactor gearboxes handling nitric and sulfuric acid mixtures

Packing seal lubricants for chemical injectors for oil and gas area applications

Lubricant/coolant for double mechanism seals of centrifugal pumps handling corrosive, harsh chloride slurries.

Some specific reports observed forth performance advantage in industrial applications are presented as follows.

#### **1. Refrigeration Compressor**

PAOs have also been used in ammonia and fluorocarbon refrigeration compressor for the reason that of their low pour points. Other performance advantage explained for PAO fluids consist of lower operating temperature and less equipment vibration. Bloch. And Williams discuss several other benefits that high film strength synthetic lubricants offer over different lubricants. Using process plant applications as examples; these authors found and showed that two significant advantages of using high film strength synthetic lubricants are lower operating temperatures ( $> 20$  °C) and decreased vibration. These two performance advantage raised the life of high torque worm speed reducers by 200-300 % and complete oil replacement intervals by a factor of 4 in one application. In other relevance, in addition to decreased operating temperature and vibration levels, the motor amperages were then reduced when the synthetic lubricants was used. Appropriately formulated high film strength synthetic lubricant based on diesters, PAOs, and combinations of these base stocks can result in reduced gear and bearing operating temperature.

#### **2. Turbines**

Wind turbine gearboxes are also focus to wear and pitting fatigue failure. Water contagion can also occur. Among the many lubricant-related factors, film thickness under operating conditions must be measured in the formulation of a wind turbine lubricant. Excellent high load performance low and temperature properties are possible with a PAO-based wind turbine lubricant.

PAOs have been engaged in larger General Electric and EGT industrial gas turbines. Oils used in these function must have enhanced oxidation resistance to withstand journal heat soak temperature that can go as high as 250-300° C. Mineral oils volatilize and shape deposits, whereas lubricant made with PAOs give cleaner running performance and extensive useful life of the lubricant ( from 4-5 years up to 15 years). Mobil Industrial Lubricant has found Mobil SHC 800 for land –based gas turbines. This fluid, based on PAO, gives reliability and low maintenance over wide temperature ranges.

### **3. Hydraulic Oil Performance**

PAO provides a variety of property/ performance features and reimbursement that cannot be achieved using alternative base fluids. PAOs have excellent viscosity index and low temperature fluidity when compared to all but the most expensive base fluids. PAOs have very less volatility and excellent hydrolytic, thermal and oxidative stability comparative to many other oils.

### **4. Metalworking Performance**

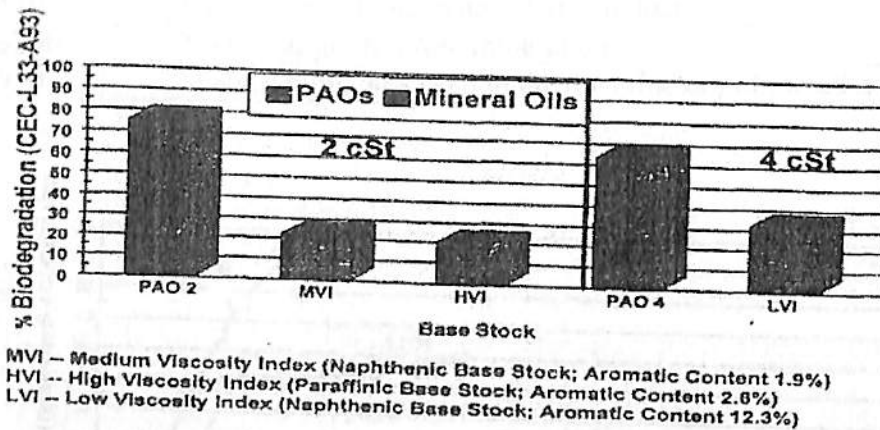
Ant seizure properties of lubricants, as considered by their maximum workable die temperature (MWT), have been noticed. The maximum workable die temperature of lubricating oils are as follows: PAO oils, 160-170° C; polybutene oil, 150° C; mineral oils 100-120° C; ester oils, 90° C. Addition to mineral oils or PAOs of phosphorus-containing excessive pressure agents improved the workable die temperature to about 300° C.

### **5. Cost Savings**

The open literature shows a number of reports of savings gathered by industrial concerns that switched from a mineral oil to a PAO-based gear or bearing oil. Table mentioned below, a short tabulation of some of these findings, explains diverse types of manufacturing and a diverse variety of applications for which the PAO-based lubricants were applied. The annual savings for these companies varied from \$12,000 to \$ 98,000. The largest noted savings in the respective table found (\$98,000/year) was achieved when PAO-based gear oil was used on the felt roll bearings in a paper mill. The high speed of the enormous rolls in a paper mill is critical to their competitive procedure, and the use of PAO-based fluids is becoming an important piece of the overall strategy for cost-effective operation.

**Table 10 - Savings with PAO-Based Gear Oils**

Company type	Application	Annual savings
Soybean processing	Aeration blower	\$2100/unit
Steel mill	Fly ash blower shaft thrust bearings	\$77,000
Copper wire	Line gears	\$19,000
Aluminum cans	Gear reducers	\$35,000
Paper mill	Felt roll bearings	\$98,000
Pharmaceutical	Gear reducers	\$70,000
Plastics	Bearing circulation system	\$12,000
Manufacturing	Various	\$80,000



**Figure 9 – Biodegradability of base stocks poly( $\alpha$ -olefins) versus equiviscous material oils; MVI, medium viscosity index (naphthenic base stock, aromatic content 1.9%); HVI, high viscosity index (paraffinic base stock, aromatic content 2.6%); LVI, low viscosity index (naphthenic base stock, aromatic content 12.3%).**

**D. Application Sensitive to Health and Environment Issue**

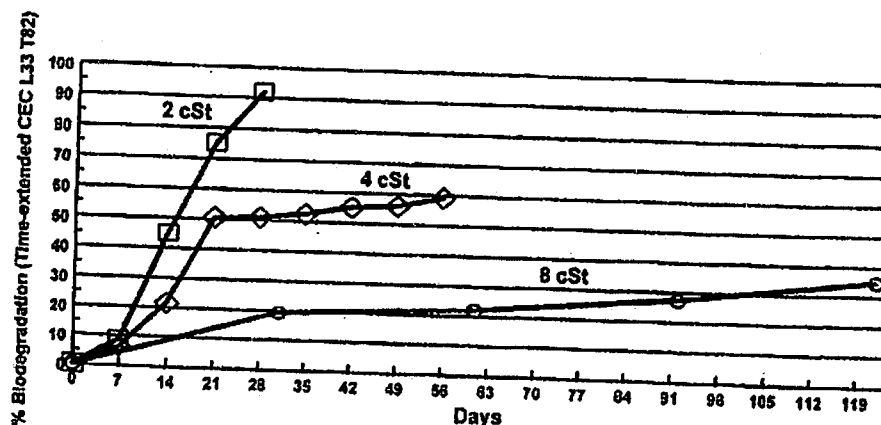
**1. Food Contact**

PAO base stocks are clean, saturated hydrocarbons. They hold no aromatics (except for small quantities in the 40 and 100 cst fluids produced by Mobil) and no functional group. As such, the toxicity is predictable to be as low as or lower than the most highly distinguished white mineral oils.

The PAOs have Food and Drug Administration (FDA) sanction for use in both “indirect” and “incidental” food contact applications. They go down within the definition of a white mineral oil according to the rules of Federal Regulations. The applications for which FDA approval is essential, and for which PAO is qualified.

**Table 11**

CFR section	Application
175.105	Adhesives
176.200	Defoaming agents used in coatings
176.210	Defoaming agents used in the manufacture of paper and paperboard
177.2260	Production of resin-bonded filters
177.2600	Rubber articles(plasticizers) intended for repeated use
177.2800	Production of textiles and textile fibers
178.3570	Lubricants with incidental food contact
178.3620b	Technical grade white mineral oil
178.3910	Surface lubricants used in the manufacture of metallic articles



**Figure 10 – Biodegradability versus time for PAO fluids**

## 2. Cosmetics and Toiletries

PAO fluids are nontoxic when given in words to rats. The poisonous dosage for 50% of the test subjects (LD<sub>50</sub>) is greater than 5g/kg of body weight. PAOs are also found nonirritating to the skin and eyes of test animals, and they are not projected to induce sensitization reactions. They have low vapor pressure and therefore are not at all hazardous if inhaled. Subjectively, PAOs are found to have a better “feel” on human skin than white mineral oils. For all these foresaid reasons, a little but growing market for PAO is developing in the cosmetics industry. A national brand of lipstick contains PAO as a chief component and in



Europe PAOs (polydecene) can be observed in a range of cosmetics products such as makeup removers, shower, body oils and bath oils, and makeup.

### **3. Offshore Drilling**

Policies on the marine toxicity of fluids used to lubricate the drill head in offshore drilling operations are getting tighter, particularly in North Sea. PAO fluids have been used as a base stock for synthetic-based drilling fluids in various offshore applications. The main goal of these fluids is bit cooling, well bore cleaning and lubrication, and shale stabilization. The release of cuttings using synthetic-based muds is considered not as much of harmful to the marine environment. PAOs provide excellent marine toxicity values. This technology, developed in the early 1990s has been moved by alternative technologies. Leading alternative technologies contain linear  $\alpha$ -olefins and isomerized olefins.

### **4. Miscellaneous**

Other environmentally sensitive areas for which PAO fluids are being evaluated are logging operations (chain saws), marine outboard engines, and hydraulic systems for large farm machinery. In addition to low toxicity, it is important that fluids used in these applications exhibit biodegradation and low levels of bioaccumulation. Preliminary evaluations indicate that PAOs do not bioaccumulate and that their rate of biodegradation is faster than that of mineral oils of comparable viscosity. On the other hand, the rate of biodegradation is slower than for some ester-based drilling muds also being evaluated for this application.

### **5. Military Application**

The most basic application for PAO fluids were in the military. MIL-H-83282 is a requirement for a hydraulic fluid for jet aircraft. The specification was made around an experiment 4.0 cst decene-based PAO formed by Mobil in late 1960s. The requirements contained extreme low temperature fluidity as well as high fire and flash point values. The concluding requirement was to minimize the risk of loss due to fire in the occurrence that a hydraulic line was severed by gunfire. MIL-H-83282 are leftovers an important military fluid today.

### **6. Space Application**

Precision spacecraft mechanisms need critical selection of lubricants to maximize consistent performance in space, where low or no maintenance is the rule. Communication, global surveillance, metrological, and navigational space craft possess a variety of moving mechanical assemblies (MMAs). These mechanical subsystems have become life-limiting for several spacecraft. Most complications have been lubricant-related, including loss of bearing contact and/or chemical degradation. Outcomes of recent studies support the use of formulated poly ( $\alpha$ -olefin) and oils and grease for most high cycle precision bearings.

## VI. MARKETS AND PRODUCTION CAPACITIES

By the end of 1990, world PAO demand had grown to 188.4 million (MM lb). This volume is a remarkable 14 times of that in 1975 and still represents less than 0.05% of the total world lubricant base stock market at that time. By the end of 1993, world PAO demand had grown to 260 MM lb. U.S.S capacity, as of June 1, 1993, was reported at 287 MM lb and was predicted to grow to 458 MM lb/yr by the year 2000.

During 1975-1980, demand for PAO grew at 33% per year. Synthetic engine oils were a novelty on the market during this period, and they were emerging from a base near zero. Growth however slowed during the 1980-1985 period to around 7%. Some of the early product competitors to the market were improperly formulated and the subsequent poor performance added some stigma to the use of synthetics. The 1985-1990 half-decade saw a sturdy new interest in synthetic lubricants because of the enactment of stringent specifications and governmental regulations that were challenging to meet with mineral oil base stocks. The growth rate for PAO during this period was approximately 19% per year.

### A. Demand by Segment and Region

Large growth for the PAO market is predicted to continue in the foreseeable future. Table below depicts the expected rate of growth for PAO into the automotive, military, and emerging market segments. The total market was expected to grow from 185 MM lb in 1990 to 450 MM lb in 1995—an annual growth rate of nearly 20% per year.

Although the PAO markets in 1990 were approximately of same proportions in Europe and North America, the breakdown by segments was largely different. The European market was driven mainly by the automotive demand, whereas the North American market was more balanced. In Europe, 78% of the PAO demand was for the automotive sector, while the remaining was for industrial applications. In North America, the automotive and industrial markets each took about 38% of the PAO, while the military used 17%. The remainder went into “emerging” markets.

**Table 12 - PAO Market Segment**

	<b>1990</b>	<b>Predicted 1995</b>	<b>Predicted growth rate</b>
<b>Segment</b>	<b>(MM lb)</b>	<b>(MM lb)</b>	<b>(% /year)</b>
Industrial	55	100	13
Automotive	110	230	18
Military	15	20	6
Emerging	5	100	85
<b>Total</b>	<b>185</b>	<b>450</b>	

Table below depicts a breakdown of PAO market growth by both segment and region. It should be taken into account that the 1995 forecasts expected the convergence for demand distributions by segment for PAO in Europe and North America. North America in fact started to catch up with Europe in the automotive applications area while Europe began catching up with North America in industrial applications. Both continents undertook rigorous development of the "emerging" segments. Precise numbers for market segment for 1995 were not accessible to the authors at the time of publication, however, overall market growth and inclinations are consistent with the predictions made earlier.

**Table 13 - PAO Market Segment Growth by Region**

Region and Segment	1990 (MM lb)	Predicted 1995 (MM lb)	Growth rate (% / year)
North America			
Automotive	35	100	23
Industrial	35	60	11
Military	15	20	6
Emerging	5	40	51
Total	90	220	
Europe			
Automotive	70	110	10
Industrial	20	40	15
Military	--	--	--
Emerging	--	60	N/A
Total	90	210	
Far East			
Automotive	4	15	30
Industrial	1	5	38
Military	--	--	--
Emerging	--	--	--
Total	5	20	

The developments of markets and applications for PAO have been mainly confined to North America and Europe. In 1990 the Far East accounted for about 2.7% of the demand for PAO. But between 1990 and 1995, the demand of PAO in the Far East grew at an annual rate of about 30% -- suggestive of the growth in the West during 1975-1980.

### **B. Emerging Markets**

A considerable portion of the growth being forecast for PAO has been labeled as "emerging" markets. The term "emerging" is used to designate application areas where there is a high scope for PAO to capture a part of the market now using other types of fluids.

Table lists seven areas in which PAO fluids and formulations are ongoing development to fulfill specific requirements not being fulfilled by the fluids currently in use. The three major factors for shifting from the current functional fluid to PAO are cost, performance, and toxicity.

**Table 14 -**

Product line	Current volume(MM lb)	Fluid type	Driving force
Brake fluid	440	Polyethylene glycol/silicones	Cost and performance
Textile	25	Silicones/ WMO	Cost and performance
Dielectric fluids	90	Mineral/silicones/PCB	Cost /performance/toxicity
Personal care	150	WMO/ esters <sup>a</sup>	Toxicity
Refrigeration	45	Polyalkyl glycols	Performance
Polymer	200	WMO <sup>a</sup>	Toxicity/ performance
Shock absorbers	110	Mineral	Performance
Total	1060		

<sup>a</sup>WMO, white mineral oil; PCB, polychlorinated biphenyl.

### **C. PAO Production Capacity**

At the fall of 1990, the worldwide production capacity for PAO was 325 MM lb/yr. Sales for 1990 were 57% of production capacity, which signified a significant reversal of demand/supply situation of the mid-1980s. Because of the shortage of PAO available earlier, formulators were required to find alternative (sometimes even less satisfactory) solutions for their performance requirements. There was a strong and comprehensible hesitancy among equipment manufacturers, formulators, and end users to place themselves in an unwarranted supply situation. As a result of the exceptional supply situation that now exists, there is a new gush of activity in the development of new markets and applications for PAO fluids.

Table underneath is a summary of the PAO producers and their capacities in 1990. Ethyl Corporation brought their 80 MM lb/yr plant in Feluy, Belgium, on-stream in January 1991. As mentioned earlier, in 1994 Ethyl split off Albemarle as a separate company, which owned and operated the PAO business until March 1996, when Amoco purchased the  $\alpha$ -olefin and PAO business from Albemarle. In 1991 Neste brought their 45 MM lb/yr plant in Berigen, Belgium, on-stream. PAO production capacities as of 1993 are briefed in table below. A summary of synthetic lubricants including markets and consumption for PAOs have been published, and price-performance data are available as well.

**Table 15 -**

<b>Manufacturer</b>	<b>1990</b>	<b>1993</b>	<b>Predicted 1996</b>
Neste	0	66	62
Uniroyal	0	0	4.4
Ethyl	170	0	0
Mobil	80	157	224
Amoco	0	0	249
Albemarle	0	256	0
Chevron	55	88	53
Exxon	20	0	0
<b>Total</b>	<b>325</b>	<b>567</b>	<b>592.4</b>

#### **D. Competitive Products**

Highly refined mineral oils compete with PAO in some performance characteristics. These mineral oils categorized in three categories, as explained in the following subsections.

##### **1. Very High Viscosity Index (VHVI) oils**

The leading product derived from crude oil sources is Shell Oil's patented extra high viscosity index (XHVI) oil. It is produced in France and Australia from a special cut of refinery slack wax by a severe hydro-cracking procedure. Shell's capacity is 150 MM lb/yr. Shell is presently manufacturing XHVI base stocks from syngas in Malaysia. The product shows very good performance characteristics, but it is lacking relative to PAO in both low temperature properties and volatility.

Petro Canada has lately started the production of a 100 MM gal/yr base oil plant in Ontario. This Production consists of a series of severely hydro processed mineral oils (VHVI fluids) under the name of Phoenix. These normally have higher pour point and higher NOACK volatility as compared to the equi-viscous PAOs, but are improved over conventional mineral oil base stocks.

BP presently manufactures LaVera Hydrocracked Residue (LHC) fluids in LaVera, France. LHC fluids are available in 3, 4, 6, and 8 cst grades. Processing consist of hydro cracking of a middle distillate stream, followed by vacuum distillation and a dewaxing step. These stocks are wax isomerates that are extremely isoparaffinic.

Chevron has also lately declared that it will produce unconventional base oil (UCBOs) at its lubricant base oil facility in Richmond, California. These new base oils are expected to be in the range of 115-135 VI.

Conoco and Pennzoil have announced a joint venture, Excel Paralubes, to produce 18,000 barrels of base oil per day at Conoco's plant in Lake Charles, Louisiana. These materials are imperiled to Chevron's iso-dewaxing process to produce higher quality base stock. Under the name

Hydroclear™, Conoco is marketing a new line of clear lube oils produced using hydrocracking technology.

The base oil plant of Yukong Ltd, in South Korea produces VHVI base stocks using a combination of hydrocracking and catalytic dewaxing process developed by Yukong with Raytheon Corporation.

## **2. High Viscosity Index (HVI) Oils**

HVI base stocks are transitional in properties amidst the VHVI fluids and conventional solvents-refined oils. HVI oils are manufactured by a process that includes hydrotreating, redistilling, and solvent refining. HVI fluids were first produced by British Petroleum in 1976 and are now produced by BP at LaVera and Dunkerque in France. HVIs are also produced by Modrica in Yugoslavia and DEA in Germany. HVI fluids are cheaper than either PAO or VHVI fluids, but 1.4-2.0 times more material is usually required to blend with an off-spec mineral oil to make a formulation of 10W-30 specifications.

Exxon has begun providing screening samples of its new RHC™ (raffinate hydro-conversion) base stocks, which it plans to produce at its Baytown, Texas refinery in 1999. These high viscosity index oils will be in the range of 105-120 VI.

## **3. Poly (internal) olefins (PIO)**

PIO fluids like PAO fluids are manufactured by the oligomerization of linear olefins. The olefins used for PIO manufacture, however, are derived from the cracking of paraffinic base stock. The mineral olefins are more difficult to oligomerize than the  $\alpha$ -olefins derived from ethylene chain growth, and the product have Viscosity that are 10-20 units lower than those of comparable PAOs.

## **VII. CONCLUSION**

A number of forces will lead the growth of high performance functional fluids for the next decade and further future. These forces are derived from diverse societal needs, but they have a common goal rooted in the uniquely human belief that there must be a better way to do whatever it is that has to be done. Some of these forces and the consequences they imply the growth of PAO fluids include the following.

### **A. Regulatory**

U.S. regulations for corporate average fuel economy (CAFÉ) are having a significant effect in both the design of new automobiles and the lubricant requirements and recommendations for them. To meet the fuel economy standards, which will now include a cold-start cycle specification, the OEMs are being forced into recommending SAE 5W multigrade crankcase oils. In addition, increased emphasis on aerodynamics results in higher engine operating temperatures, which affects not only the crankcase lubricant but also the transmission fluid, the gear oils, and the greases. All these factors will require fluids with lower low temperature viscosity coupled with lower volatility, higher thermal and oxidative stability, higher heat capacity, and higher heat conductivity.

Regulations in areas of consumer's protection, worker safety, and the environment are becoming increasingly stringent in their requirements for nontoxic, nonhazardous, environmentally friendly products. Regulatory agencies are beginning to recognize potential toxicological problems associated with white mineral oils. PAOs are being put forward as high performance, safe substitutes.

### **B. Performance and Cost-effectiveness**

The need for improved performance remains a critical factor in the drive towards increased usage of PAO-based lubricants and functional fluids. In many applications mineral oil based products either cannot meet the more stringent requirements or are only marginally satisfactory. The use of PAO for blending with marginal base stock to bring them into specification is increasing.

Fleet operators, who are much more sensitive to cost-effectiveness than the general public, will continue to increase their usage of synthetics as they recognize the potential long-term savings.

Operators of large industrial machinery are beginning to recognize the increased cost-effectiveness of lubricant with PAO-based products. Machines operate at lower temperature, are less subject to wear, require less maintenance and downtime, consume less oil, and operate longer between lubricant drain cycles. The value of PAO-based products for the lubrication of heavy-duty, off-road mobile equipment is also being recognized, especially where routine maintenance is difficult.

### **C. Original Equipment Manufacturers (OEMs)**

The diversity and uneven regional availability of mineral oil base stocks hamper standardization based on mineral oils. In application for which performance requirements are rigorous, there will be a shift by OEMs to ensure consistency by requiring synthetic fluids.

Industrial and automotive OEMs are driven by the consumers and by the competition to extend warranty periods. At the same instance, OEMs are under pressure to decrease the required amount of maintenance and downtime. Both concerns may be satisfied by switching from

mineral oil to PAO-based fluids. General Motors used a full-synthetic, PAO-based oil as a factory-fill and recommended crankcase fluid for the first time when it presented the 1992 Chevrolet Corvette. Today, fully synthetic PAO-based oil is still suggested for the high performance vehicle.

The latest tendency to answer consumer convenience and the protection of equipment from unintentional contamination of the working of the working fluids is the "fill-for-life" concept. General Motors is doing research on a "fill-for-life" PAO-based automatic transmission fluid for its future models.

#### **D. Petroleum Companies and Blenders**

Lubricant producers have traditionally had low profit margins. Base stock prices have been closely related to crude oil prices, and the selling price for finished fluids has always been linked to base stock costs. Lubricant companies have started to recognize that high performance; high image products based on PAO provide the opportunity for higher selling prices and increased margins. European companies have been the leader in this concern, but North American companies are anticipated to catch up. While Mobil Oil has been the leader in the United States with Mobil since the mid-1970s, most of the major lubricant producers have announced, or planned to announce, PROLOGUE of full-synthetic motor oils to the market.

Another big factor in the forecasted growth for PAO is the recognition that there are inadequate high quality base fluids to satisfy new product requirements. PAOs will be used to blend mineral oil stocks into specification. Some of these products will be sold and marketed as "part-synthetic" oils at a price between the top tier mineral oils and the "full synthetics." In other cases, the blender or formulator will use PAO in an "in again-out again" basis, depending on the accessibility of mineral oil base stocks of suitably high quality. In these cases, consumer will never know that they have purchased a "part-synthetic."

#### **E. Consumer**

The role of the consumer is invaluable to the growth of PAO fluids. Manufacturer's recommendations will have a little influence if the consumer does not pay attention to them. Studies show that the traditional attitude in the United States (i.e., that all oils are "pretty much the same") has started to change. Consumers are becoming more conscious of issues such as fuel economy, cleaner air, higher performance, lower maintenance, and longer vehicle life. All these apprehensions, along with the increased availability of oils to meet the demand, are expected to lead to shift a part of the consumer population toward the premium synthetic oils.



# **CHAPTER 2**

## **Comparison of Synthetic Fluids**

### **I. PROLOGUE**

The circumstances of the specific frictional contacts, also those in which environment have to be taken into consideration are needed for determining the application of lubricants. Both these influencing aspects result in the total complex of the requirements to which lubricants are exposed to and all these requirements must be satisfied if a satisfactory service life is to be obtained. Ranges and conditions of lubricants are decided by the extent and importance of the individual requirements. If a single requirement exceeds the limit application of a certain fluid, its use will be certainly questionable, inconsiderate of whether all other requirements are met easily.

### **II. REASONS FOR CHOOSING SYNTHETIC FLUIDS**

Irrespective the limit of application of fluids, physical and chemical effects have to be considered. The physical effects are characterized by temperature and pressure. The solidification of a fluid at low temperature and high pressure limits its application, and so does its evaporation at high temperatures and low pressures.

The characteristics of oxidation and radiation influences, both are affected by temperatures. Two conditions favor the decision to use a synthetic fluid instead of a mineral oil are:

The expected or required property cannot be exhibited by mineral oils, even by those containing additives.

The extent of the desired or required property cannot be met by mineral oils, even those containing additives.

Mineral oils can be poorer in comparison to certain synthetic fluids based the following properties or property complexes:

- thermal stability
- oxidation stability
- viscosity-temperature behavior
- flow behavior at low temperatures
- volatility at high temperatures
- temperature range of application
- radiation stability
- ignition resistance

No synthetic fluid exhibits all properties in a greater manner to mineral oils. Generally some inferior properties have to be taken into consideration. Synthetic fluids may be poorer to mineral oils with respect to the following properties:

- Hydrolytic behavior
- Corrosion behavior
- Toxicological behavior
- Compatibility with other design materials
- Miscibility with mineral oil
- Compatibility with seal materials
- Additive solubility
- Availability in general, or in certain viscosity grades
- Price

Again, it should be noted that no synthetic fluid exhibits all properties in an inferior manner to those of mineral oils. As a result, some synthetic fluids that contain poorer performance in a certain applications may have better performance in some other areas.

Thus, the following point of view must also be thought upon. Several advantageous properties may be related unavoidably with less adequate properties. For example, behavior under mixed-film lubrication conditions is largely controlled by mutual interactions between the lubricant molecules and the surface of the frictional contact, which are sequentially characterized by the chemical and physical reactivity of the fluid. But various synthetic fluids have good chemical and physical stability, therefore good oxidation and thermal stability too.

### **III. FIELDS OF APPLICATION AND MARKET SHARE**

Synthetic and partly synthetic lubricants are implied in automotive, aviation, and industry application. Table 1 depicts few of the main fields of applications where synthetic lubricants show advantages over mineral oil-based lubricants. Table 2 shows the consumption of synthetic and partly synthetic lubricants in the past and depicts demand for these lubricants for the future;

this data apply for Western Europe. From table 3 it's quite obvious that the market share of synthetic fluid based lubricants probably will not cross 7-8% of the total lubricants market.

**Table 16: Possible Areas for Applying Synthetic Lubricants**

<b>Automotive</b>	<b>Aviation</b>	<b>Industry</b>
Engine oils	Turbine oils	Gas turbine oils
Four-stroke oils	Piston engine oils	Gear oils
Two-stroke oils	Hydraulic fluids	Bearings and circulation oils
Gear oils	Lubricating greases	Compressor oils( gas, air, refrigeration)
Brake fluids		Hydraulic oils
Lubricating greases		Metalworking fluids
		Heat transfer and isolating oils
		Lubricating greases

**Table 17: Demand in Western Europe for Synthetic Lubricants (1000 tons/yr)**

<b>Area of Application</b>	<b>1985</b>	<b>1990</b>	<b>1995</b>	<b>2000<sup>a</sup></b>
<b>Automotive</b>	45	90	130	166
Four-stroke engine oils	3	7	10	10
Two-stroke engine oils	2	4	6	8
Gear oils	6	4	4	6
Lubricating greases	56	105	150	190
<b>Aviation</b>	9	10	11	13
Turbine oils	1	2	2	2
Piston engine oils	1	1	2	3
Hydraulic oils	--	--	--	--
Lubricating greases	11	13	15	18
<b>Industry</b>	1	1	1	2
Gas turbine oils	8	15	21	27
Gear, bearing, and circulating oils	5	10	15	15
Compressor oils	23	25	29	34
Hydraulic oils	25	35	40	43
Metalworking fluids	2	4	6	7
Lubricating greases	1	2	3	4
Heat transfer and isolating oils	65	92	115	132
<b>Total</b>	<b>132</b>	<b>210</b>	<b>280</b>	<b>340</b>

<sup>a</sup> Estimated

**Table 18: Proportion of Total Lubricants Market Devoted to Synthetic Lubricants**

1985	1990	1995	2000 <sup>a</sup>
< 2.0%	3.5%	5.0%	7.-8.0%

<sup>a</sup> Estimated

#### IV. CLASSIFICATION OF SYNTHETIC FLUIDS

Synthetic fluids can be classified depending on their chemical composition. Table 4 shows the elementary types of synthetic fluids that can be distinguished. The other criterion of classification, particularly for making the distinction between mineral oils and synthetic fluids, is the production process. Mineral oils are produced by distillation and raffination, whereas synthetic fluids are obtained by chemical reactions. The chemical structure of synthetic fluids suggests a third criterion for their systematic classification.

**Table 19:**

Synthetic fluids	Composition
Synthetic hydrocarbons	C,H
Poly ( $\alpha$ -olefin)	
Alkylated aromatics	
Monoalkylbenzenes	
Dialkylbenzenes	
Polyalkylene	C, H, O
Carboxylic acid esters	C, H, O
Dicarboxylic acid esters	
Neopentyl polyesters	
Phosphoric acid esters(phosphate esters)	C, H, O, P
Silicon oils	C, H, O, Si
Silicon oils	
Polysilicons oils(siloxanes)	
Silicate esters	
Polyphynyl ether	C, H, O
Polyfluoroalkyl ether(alkoxyfluro oils)	C, F, O
Chlorofluorocarbons, chlorotrifluoroethylenes	C, F, Cl
Polymethacrylate/poly( $\alpha$ -olefin) co-oligomers	C, H, O

**Table 20: Classification of Mineral Oils and Synthetic Fluids According to Production Process**

Mineral oils, produced by distillation and refining		Synthetic fluids, produced by chemical reactions	
Conventional technologies	Modern technologies	Synthetic hydrocarbons	Other synthetic fluids
Acid refining	Hydrotreating	Poly( $\alpha$ -olefins)	Dicarboxylic esters
Solvent extraction	Hydrocracking	Polyisobutenes	Neopentyl polyesters
Dewaxing		Dialkylbenzenes	Polyalkylene glycols
			Phosphate esters
			Silicon oils
			Polyphenyl ether
			Perfluoroalkyl ether
			Chlorofluoroalkyl ether
			PMA/PAO co-oligomers

## V. COMPARISON OF CERTAIN TEMPERATURE-RELATED PROPERTIES

The temperature limits of mineral oils are between 100 and 150° C for oxidation and between 350 and 450° C in case thermal stability is considered.

The relatively small impact of oxidation inhibitors further increased the service temperature and is clearly recognized. If the oxidation can be avoided, much higher service temperature can be applied to mineral oils. The limiting temperatures are described by the limited thermal stability of the oxidation inhibitors.

The Flash Point and Pour Points of some of the synthetic Lubricating Oils is shown below:

**Table 22:**

Fluid	Temperature (° C)	
	Flash Point	Pour Point
Mineral oils	200-300	0 to -60
Poly( $\alpha$ -olefin)	200-350	-20 to -60
Polyalkylene glycols	200-260	-30 to -50
Perfluoroalkyl ether	-----	-20 to -75
Polyphenyl ether	230-350	+20 to -20
Diesters	200-270	-50 to -80
Phosphate esters	100-260	-10 to -60
Silicon oils	230-330	-10 to -100

Silhydrocarbons	270-290	-5 to -15
Silicate esters	180-280	-50 to -70

## VI.COMPARISION OF SOME PROPERTY GROUPS

For several application reasons, the most appropriate and expedient way to select the optimum synthetic fluid is the comparison of various property groups to satisfy the requirements of special tribologies contacts. This is mostly done (comparison) for better viscosity, stability, and lubricity properties.

Following tables simultaneously compares behaviors like thermal, oxidative, hydrolytic, and volatility of synthetic fluids and of mineral oils. Barely any single fluid exhibits excellent, or even very good behavior, regarding the four mentioned properties. The next table illustrates a similar kind of comparison for low temperature fluidity, viscosity index, and pressure viscosity properties. Poly( $\alpha$ -olefin), esters and some other silicon-containing fluids show very good or even excellent behavior on all properties, the third table compares wear protection properties, without and with additives, and fatigue life behavior. Also, it is fairly evident that no single fluid exhibits very good or even excellent coverage to all requirements.

**Table 23:**

Product	PROPERTIES			
	Thermal	Oxidative	Hydrolytic	Volatility
Mineral oil(paraffinic)	Good	Fair	Excellent	Poor/fair
Poly( $\alpha$ -olefin)	Very good	Very good	Excellent	Very good
Diesters	Good	Very good	Fair	Good
Polyol esters	Good	Very good	Fair	Good
Polyalkylene glycols	Good	Good	Good	Good
Phosphate esters	Fair	Good	Fair	Fair/good
Silicones	Very good	Good	Excellent	Excellent
Alkylbenzenes	Good	Good	Excellent	Good
Fluorocarbons	Excellent	Excellent	Good	Poor
Polyphenyl ethers	Excellent	good	Excellent	Good
Silicate esters	Very good	Good	Fair/poor	Good
silhydrocarbons	Excellent	Very good	Excellent	-----

\*This table depicts the relative evaluation of viscosity properties for different synthetic fluids.

**Table 24:**

Product	PROPERTIES		
	Low temperature fluidity	Viscosity index	Pressure-viscosity
Mineral oil (paraffinic)	Fair/good	Good	Good
Poly( $\alpha$ -olefins)	Excellent	Very good	Good
Diesters	Very good	Very good	Very good
Polyol esters	Very good	Very good	Very good
Polyalkylene glycols	Very good	Very good	Very good
Phosphate esters	Fair/good	Fair/good	Very good
Silicones	Very good	Excellent	Excellent
Alkylbenzenes	Good	Very good	Good
Fluorocarbons	Fair	Fair	Fair
Polyphenyl ethers	Poor	Fair	Poor
Silicate esters	Excellent	Excellent	Very good
silahydrocarbons	Excellent	Excellent	-----

\*Again, the next table depicts the Relative Evaluation of Lubricity (wear protection and fatigue) of Different Synthetic Fluids.

**Table 25:**

Product	PROPERTIES		
	Natural lubricity and anti-wear	Anti-wear additives with	Fatigue life
Mineral oil (paraffinic)	Good	Excellent	Fair/good
Poly ( $\alpha$ -olefins)	Good	Excellent	Good
Diesters	Fair	Good	Fair
Polyol esters	Fair	Good	Fair/good
Polyalkylene glycols	Good	Good	Fair
Phosphate esters	Excellent	Excellent	Fair
Silicones	Poor	Fair	Fair/good
Alkylbenzenes	Good	Excellent	Good
Fluorocarbons	Fair/good	Good	Fair/good
Polyphenyl ethers	Good	Good	Good
Silicate esters	Good	Very good	Poor

## VI. ALLOCATION OF PROPERTIES TO FIELDS OF APPLICATION

The idea of using synthetic lubricants mainly depends on their specific properties, particularly compared to those of mineral oils. Considering this point of view, the advantageous properties support applications for which requirements concerning to frictional contact cannot be satisfied by mineral oils. On the other hand, some chief disadvantages of certain synthetic fluids eliminate them from several specific fields of application. This allocation of properties to application is tabulated below for poly ( $\alpha$ -olefin):

Table 26:

Advantages	Especially Suited for
• Good flow properties at low temperature	<ul style="list-style-type: none"> <li>• Engine oils</li> <li>• Compressor oils</li> <li>• Hydraulic oils</li> <li>• Gear oils</li> <li>• Greases</li> </ul>
• High thermal and oxidative stability	
• Low evaporation losses at high temperature	
• High viscosity index	
• Good friction behavior( mixed film)	
• Miscibility with mineral oils and esters	
• Good hydrolytic stability	
• Good corrosion protection	
• Not toxic	
<b>DISADVANTAGES</b>	
• Limited biodegradability	<ul style="list-style-type: none"> <li>• High performance gear oils</li> <li>• Fast biodegradable oils</li> </ul>
• Limited additive miscibility	

To depict the distribution for other synthetic fluids, the table below shows the main fields of application for each of them.

Table 27:

Synthetic oil type	Main applications
<b>Synthetic hydrocarbons</b>	
• Poly ( $\alpha$ -olefin)	Engine oils, industrial lubricant (compressor, hydraulic, and bearing oils)
• Polyisobutenes	Metal-forming oils, two-stroke engine oils, electrical isolation oils
• Alkylated aromatics	Low temperature oils for gears, engines, hydraulics
• cycloaliphates	Friction gear oils (due to high coefficient of friction)
<b>Organic esters</b>	
• Diesters	Turbine oils, mixing components for poly ( $\alpha$ -olefin)
• Polyolesters	Turbine oils, compressor, hydraulic, and gear oils
<b>Polyglycols</b>	



• Water soluble	Brake fluids, metalworking oils, worm gear oils, fire resistance hydraulic fluids
• Non-water soluble	Worm gear oils
<b>Others</b>	
• Phosphate esters	Fire resistant hydraulic fluids, gas turbine oils
• Silicone oils	High temperature hydraulic fluids, brake fluids, compressor oils
• Halogenated fluids	Extremely fire-resistant hydraulic oils
• Polyphenyl ethers	Radiation-resistant lubricants, heat transfer fluids

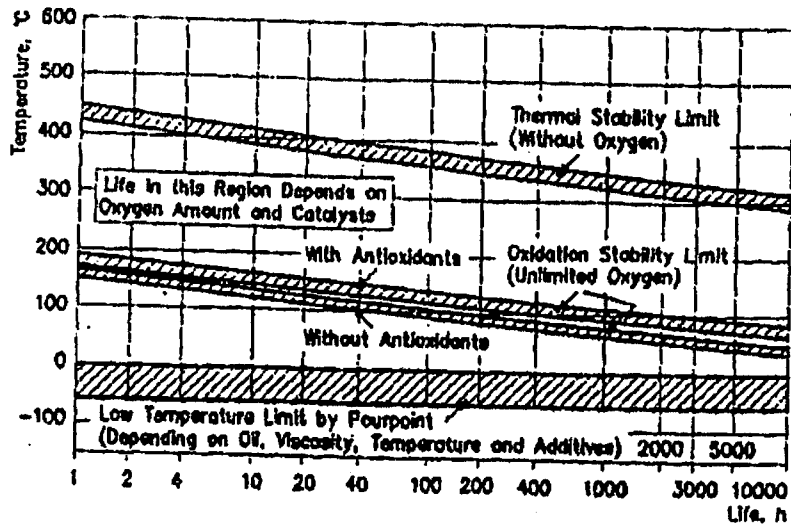


Figure 11- Temperature limits for mineral oils

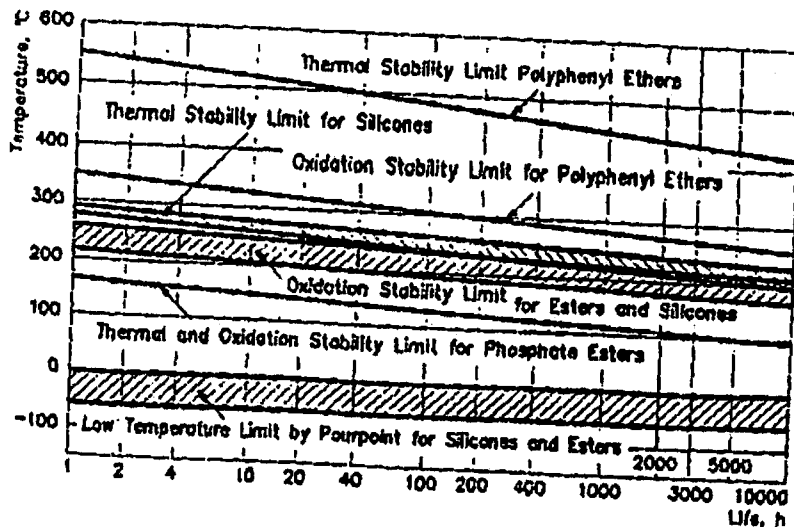


Figure 12 – temperature limits for some synthetic oils

# CHAPTER 3

## Industrial Trends

### I. PROLOGUE

The industrial sector of the market for functional fluids is vast. In many divisions of the market, it is taken broadly to include all sectors excluding those associated with transportation and military. Within the metalworking industry, water based fluids are often referred to as synthetic fluids. These may however be described as highly refined mineral fluids.

Currently the use of synthetic fluids within the industrial market is relatively small. In volume terms, about 6% of the U.S. industrial market for oil and functional fluids is based on synthetic fluids. In Europe about 5% of industrial of oil and functional fluids are either synthetic or semi synthetic. The share of the market held by synthetic fluids will increase, but only gradually, and only as the use of a synthetic fluid can be justified in terms of improved efficiency, improved quality or if concerns over safety or environment require their use. Synthetic fluids generally will increase their presence in the market through gradual application in the niche areas. However, it is possible that in some areas legislative action will, either directly or indirectly, force a wholesale change in fluid type from a mineral oil to a synthetic. This already has been seen in the lubricants for use in R-134a compressors and the development of drilling mud based on synthetic base stocks.

Any growth in the market share of synthetics have to be viewed within the context of the global demand for lubricants, which is reported to have shrunk from 38.4 million tons in 1990 to 36.7 million tons in 1994. Among the factors given for this decrease was recognition that "each advance in lubricant performance and equipment efficiency carries the seed of lower demand, as less lubricant can do the job for a longer period of time". For the future, lubricant growth was put at something less than world economic growth was put at something less than world economic growth – perhaps 1.4% versus total economic growth of 3.8%.

### II. MARKET NEEDS

#### A. Cost – Performance balance

Cost versus performance is the key to the development synthetic fluids based products. In general, the synthetic fluids will be more expensive than its mineral oil based competitor. Therefore, the use of a

synthetic fluid in place of a mineral oil maybe justified only if the synthetic's performance offsets its higher price.

Many industrial processes, along with the associated equipments, are being developed to operate at a higher temperature. Higher temperature can allow faster processing, hence the realization of gains in productivity and greater efficiency. Alternatively, products of superior quality may be produced. These higher temperatures are leading to a demand for less volatile and more thermally and oxidatively stable fluids. Many synthetic fluids show improved thermal and oxidative stability over mineral oils. These also tend to show, for a given viscosity, lower volatility and higher viscosity index. For moderate increases in continuous operating temperature up to about 180°C, poly ( $\alpha$  olefins) (PAO's) or dibasic acid esters may be suitable. Beyond 180°C, up to about 215°C, poly esters or polyalkylene glycols offer improved stability. At yet higher temperatures polyphenylene oxides or perfluorinated polyethers could be required. All these fluids are capable of intermittent service at higher temperature than those given. Research into high temperature lubricants is an active area, often first stimulated by the military or transportation sector of the market rather than by the industrial sector. Research into lubricants for use in low heat rejection engines, in particular, may lead to new classes of fluids that will find eventual application in the industrial sector.

In cold conditions, low temperature fluidity becomes an important requirement. Specially refined mineral oils are capable of operation down to less than -55°C, but these are indications that these fluids are becoming less available. Synthetic fluids often exhibit good low temperature characteristics. PAOs, depending on viscosity, have pour points down to less than -65°C. For specialized applications under very cold conditions, such low temperature properties may remove the necessity for auxiliary heating systems or reduce the power needed from a starting system. More precise hydraulic control is also potentially available. In the medium term, the market for low temperature lubricants and fluids is not expected to expand greatly, but in the longer term the need to unlock the natural resources in the subarctic and possibly, if environmental factors allow, Antarctic regions, will expand this niche area.

In more general areas of application, a synthetic fluid may allow longer periods between oil drains, and the associated reductions in downtime more than pay for the higher cost in the extreme, synthetic fluids may allow the development of "fill-for-life" fluids systems that will simplify equipment design and construction by, for example, removing the need for oil drain plugs. Such simplifications can be vital elements in potential cost reduced capital costs can also be realized through the use of low flammability fluids such as silicones, poly esters, and phosphate esters.

The cost of the fluid is fundamental to the cost-performance equation, and the final choice between synthetic fluids may well be determined by the relative differences between the prices of these fluids. Relative pricing can be expected to vary with differences between the prices of these fluids. Relative pricing can be expected to vary somewhat as a function of supply/demand relationships, which will impact not only on the pricing policies of synthetic fluid suppliers but also on the costs of raw materials and production. However, for the majority of established fluids, relative prices are likely to stay broadly as they are today. The prices of developmental synthetic fluids can be expected to fall dramatically if they manage to establish themselves and economics of scale are brought into play. It also needs to be borne in mind that the price of base fluid is often a minor component of the overall cost of a finished functional fluid. There will be costs of additives, blending and packaging costs, and costs of distribution. There are

also the overheads associated with research and development and product promotion. For relatively small-volume, niche applications these costs can be very high. As volumes increase and as research and development (R&D) expenses decrease, we can expect to see a trend to lower finished fluid prices. It is also increasingly recognized that the total cost of using a particular fluid is more than just the initial fluid price and its potential life- of increasing importance will be the cost of fluid disposal.

A new perspective on the cost-performance equation is developing in various markets across the industrial sector with the implementation of preventive maintenance (PPM) programs. While the main objective of a PPM program is typically to improve equipment reliability by predicting or preventing failures, a secondary benefit is the creation of a reliable measuring/monitoring system of equipment and lubricants. The data generated from the monitoring systems will not only provide better measurement of performance, but will also provide more credible determination of long term lubricant value (rather than the typical focus on initial lubricant purchase price, as mentioned above). But more importantly, the system will provide the appropriate information to focus the users' attention on the lubricant's performance and truly create a quantifiable opportunity to sell higher performing synthetic lubricants

## **B. Environmental Acceptability**

Concern for the environment is becoming an ever-larger consideration in the selection of function fluids. Environmental acceptability is judged against various criteria, which include biodegradability, toxicity, bioaccumulation, and whether the source of the fluid is renewable. Moreover, since different protocols can give significantly different results, it is very important to define test protocols in determining environmental acceptability. When consensus is reached on specific environmental tests and appropriate methods, such as ASTM procedures, are written, those tests are used to develop classification standards for fluids based on their environmental properties. Labeling schemes have been developed in a number of countries to identify environmentally acceptable fluids. Examples are the "Blue angel" in Germany, the "White swan" in Scandinavian countries, and the "Green cross" in the United States. International organizations such as the United Nations are developing proposals for the worldwide harmonization of such schemes. We anticipate that labeling schemes and their harmonization will continue to evolve as appreciation of environmental impact of fluids becomes better understood and as test protocols become better developed.

In many cases a particular synthetic fluid that is environmentally acceptable than its lower cost, mineral oil based competitor and at the same time will be technically superior to vegetable-based oils or water-based fluids. New legislation and associated regulation can force a market to switch to new fluid types, even when legislation has driven polychlorinated biphenyl based fluids out of the market. This trend is expected to increase in future. Environmental acceptability is measured against a number of criteria, and in the following sections a brief review of the major factors is given.

### **1. Biodegradability**

*Biodegradability is generally regarded as a favorable fluid characteristic from an environmental standpoint. The rationale is that such will readily break down in the environment to nontoxic, simple*

compounds, ultimately, in many cases, carbon dioxide and water. Accumulation of fluids in the environment is limited, and long term problems associated with that accumulation are avoided.

It is necessary to use the term "Biodegradable" with care. The U.S. federal Trade Commission has recently issued guidelines for making environmental marketing claims. Nearly all fluids are, to some extent, biodegradable, with the possible exception of largely inorganic fluids such as silicones. Certainly a mineral oil, given sufficient factor is the rate of biodegradation under ambient conditions. Required biodegradability must therefore be defined in terms of test ambient conditions. Required biodegradability must therefore be defined in terms of a test protocol selected to reflect adequately the conditions under which a fluid may be released into the environment. In Europe, a common protocol used to determine relative biodegradability is the CEC-L-33-A94 (previously CEC-L-33-T82) test, which was originally designed to evaluate the biodegradability of two stroke oils intended for use in marine (pleasure craft) outboard engines. This test is now being used to evaluate fluids designed for very different applications. It is unlikely that the CEC-L-33-A94 test will be accepted as the protocol for determining biodegradability in governmental regulations. For example, European Economic Community (EEC) regulations that categorize environmentally hazardous materials use Organization for Economic Cooperation and Development (OECD) protocols. OED guidelines define "ready biodegradability" and "inherent biodegradability". Ready biodegradability tests provide limited opportunity for biodegradation and accumulation and acclimatization to occur, so materials giving positive results in these tests are assumed to biodegrade rapidly in the environment. Six test methods are described that permit the screening of chemicals for ready biodegradation in aerobic aqueous media. Inherent biodegradability tests may favor biodegradation. A positive result in this type of test does not necessarily mean that rapid and reliable degradation in the environment will occur. Three OECD protocols are described to determine the inherent biodegradability. ASTM is currently investigating three tests for the U.S. market: the manometric test, the EPA shake flask test, and modified Sturm, a measure developed for the OECD. All these tests were developed and written for water-soluble materials and currently being adapted for water-insoluble materials to make the methods applicable to lubricants. We are likely to see further developments, with the newer test protocols reflecting more accurately real world conditions.

Niche markets for biodegradable fluids already are becoming established. These are for use in applications where loss of fluid to the environment might be anticipated- for example, hydraulic fluids used in mobile equipment or bar oils for chain saws. Many of these fluids are based on vegetable oils, most often rapeseed oil. The biodegradable synthetic fluid must then compete with the much cheaper vegetable oil based products and will gain significant market share only where the superior technical performance of the synthetic oil leads to a cost performance benefits.

The current classes of synthetic fluids that shows a rate of biodegradation much higher than that of mineral oils are the esters (many but certainly not all) and polyglycols.

These classes of fluids are already well established in certain application areas. Their major completion will come from vegetable oils, notably rapeseed oil. Active development of these and other classes of synthetic fluids is expected to maximize biodegradability and hydrolytic stability, well in excess of what can be obtained with the use of vegetable oil based products.

## 2. Waste disposal / fluid recycling

Concern for the environment will continue to focus attention on how industry disposes of its waste. This trend that can be expected to accelerate as the disposal of waste becomes a major problem in many industrial areas, resulting in a level of fluid management much higher than we see today. There will be increased focus on reducing the overall level of waste, and the disposal of waste will be tightly controlled. The cleanup and recycling companies will provide industry with disposal, cleanup, and recycling services. This trend will favor increased use of highly stable synthetic fluids on several counts.

First, the synthetic lubricants will offer longer service life; hence level of waste material is reduced and the frequency of recycling will decrease. Secondly, highly stable synthetic fluids may lend themselves more readily to cleanup because the level of additivation may be lower in a synthetic fluid and the degree of fluid degradation during cleanup processing may be less. The price differential between a recycled synthetic fluid and a recycled mineral oil may thus be less than that between virgin fluids. All these factors may shift the cost-performance balance in favor of the relatively inexpensive biodegradable vegetable oils, a difference that could favor synthetic fluids designed to offer good recyclability together with ready biodegradability.

## 3. Fluid toxicity

The toxicity of fluids is generally evaluated as either acute or chronic aquatic toxicity. –protocols and classifications continue to evolve. A new ASTM practice for the aquatic toxicity testing of lubricants, successfully balloted in 1996 was published in 1997, and we anticipate development of the classification of toxicity built around this methodology.

From a more general perspective, we can see that synthetic fluids can be produced to very high level of purity with minimal contamination. Many fluids are essentially composed of a very few or even a single molecular species. The toxicological characteristics of the fluids therefore can be carefully assessed, and quality standards can be maintained over time. Mineral oils are a mix of many thousands of different molecules, and different of nominally the same oil can be different in terms of detailed composition in terms of detailed composition as the crude changes and refining conditions are changed. Even with highly refined white mineral oils there are concerns over potential toxicological hazards, and we may see eventual replacement might fall to synthetic fluids rather than vegetable oils is a question of cost versus performance.

## 4. Ozone depletion

Since 1974, the world community has become concerned about depletion of the ozone layer, particularly over the southern polar region. As a result, the Montreal protocol, subsequently modified in London, set down a timetable for a reduction, and eventual elimination, of the use of fluids and gas whose molecules contain chlorine.

## 5. Global warming

Parallel with the rising concern about atmospheric ozone depletion, we see apprehension over the problem of global warming. Increased regulations to control the emissions of gases that contribute to global warming can be expected. Implicit within these trends is the continuing drive towards higher

efficiency of machinery. Higher efficiency means lower energy consumption and, when the source of energy is hydrocarbon based, ultimately a reduction in the amount of carbon dioxide released. Such regulations will impact on industry's selection of functional fluids and on their use and disposal.

### **C. Quality**

The drive for improved product quality will continue as companies seek an edge for their products. There is good reason to believe that this will result in increased use of synthetic fluids, which, because of their own properties, will allow processes to operate more consistently and in such a manner as to produce higher quality end products. Often improvements in quality will be accompanied by improvements in overall productivity. Examples can be found in the textile industry, where higher quality and more efficient production in developed countries can offset lower labor costs in the control chemistries required for the production of pharmaceuticals and certain specialty chemicals.

### **D. Safety**

In response to concerns for the environment, there will continue to be improvements in overall safety of industrial processes and operations. The major area for increasing safety factor will continue to be in the reduction of fire hazards. Low flammability fluids already have major shares of the fluid market in particularly sensitive situations such as metal casting and hot metal rolling, and in the mining industry. Many halogen containing fluids currently are being displaced from these markets because of environmental concerns. This provides opportunities for alternate fluids. In any situation where there is the possibility of a mineral leaking (260-371°C), there is a real risk of fire. In the electric power generating industry, for example, there is increased risk of fire because steam temperature have risen in a trend to replace mineral oil based turbine lubricants with lubricants based on fire-retardant fluids.

Other safety issues include reducing the amounts of oil-based mists in the atmosphere of certain work environments. The degradation of fluids to airborne smokes and mists is a related problem. Both problems have been of concern in the textile industry. A new, lower exposure limit of 0.5 mg/m<sup>3</sup> (total particulates) for workplace exposure to metalworking fluids has been recommended by the National Institute for Occupational Safety and Health (NIOSH). In the chemical industry, specialized synthetic fluids can help minimize the risk involved if the fluid should come into contact with application as heat transfer fluids in vessels containing hot oleum.

## **III. SELECTED MARKET SECTOR TRENDS**

### **A. Hydraulic fluids**

Developments in the market for hydraulic fluids are being driven by three main factors. First, there is the environmental acceptability of fluids; second, there is the development of smaller, high pressure hydraulic systems; and third, there is the issue of safety in the workplace. All these factors favor replacement of

mineral oil based hydraulic fluids by alternate systems afforded by vegetable oils, water based, and synthetic fluids.

Environmental concerns cover two areas. The first addresses the general question of waste fluid disposal. This will favor synthetic fluids, with their potential for longer service life before requiring replacement. We are likely to see increased service to industrial operations in the area of "fluid management". This will cover recommendations not only for fluids use but also well further favor the use of stable synthetic fluids in that they can be more suitable for recycling, and the relatively high costs of initial fill may be offset longer and potential recycling.

The second environmental concern addresses the fate of fluids once they enter the natural environment. For mobile hydraulic equipment in particular, non-controllable leaks of fluids into the environment pose a potential hazard. This concern has resulted in a market for readily biodegradable fluids, which will continue to develop. Most biodegradable to date have been based on rapeseed oils rather than on the more expensive synthetic fluids. Vegetable oils, however, are inherently rather poor with respect to oxidative and hydrolytic stability, and parts of this market may require a higher level of stability but still a relatively high rate of biodegradation. It appears that genetically engineered vegetable oils will go some way to meeting these requirements. Where higher performance levels are required, the more expensive, synthetic oils and how much will require a higher level of performance will depend on experience, the development of new specifications, and the relative cost performance characteristics of the finished fluids.

The development of smaller, high pressure hydraulic systems will promote the use of more stable fluids able to withstand higher temperatures, and will provide greater protection to pumps. Synthetic based fluids will show the best technical performance and will penetrate this market sector. The potential reduction in fluid volume within such a high pressure hydraulic system will also reduce the differential in cost of filling the system with a less expensive fluid and with a more expensive fluid.

For many years, the temperature characteristics of certain synthetic fluids have been put to good advantage, particularly with respect to low temperature compatibility. The lower dependence of viscosity on temperature for many synthetic fluids over conventional mineral oils can give improved "feel" to manually controlled hydraulic systems, as found on much digging and construction equipment. Operators of such equipment sense a very real difference in system response when starting from cold as opposed to warmer operation. Given that such mobile systems may also require the use of relatively biodegradable fluids, we see a further factor favoring the use of polyol ester based over vegetable oil systems, because vegetable oils have a relatively high pour point. The use of PAOs in such systems has also been discussed.

Low flammability or nonflammable hydraulic fluids find particular application in situations where fire hazard presents an unacceptable risk. The mining and steel industries are the major consumers of such fluids. Over the last 15 years, it has been noticed that the replacement of polychlorinated biphenyls (PCBs) as hydraulic fluids in the mining industry, to eliminate the ecological and toxicological hazards associated with this class of chemical. In some sectors of the market, other chlorinated materials such as chlorinated materials such as chlorinated benzyl toluene found favor as PCB replacements, but these materials have also come under increasing environmental pressure and are themselves being phased out. The major low flammability synthetic fluids used in the market today are phosphate esters and long chain polyol esters or mixtures of these fluids with mineral oils. These fluids compete with each other and with



the well established classes of water containing fluids. Polyalkylene glycols, long used in water/glycol fire resistant fluids, have also been promoted as fire resistant fluids in their own right. The key factors in determining which fluid as a hydraulic fluid, materials compatibility, price, and environmental acceptability. The degree of fire resistance required often is regulated by government authorities; hence, markets show significant geographic differences.

The trend has been for polyol esters to win market share where their level of fire resistance is acceptable. This has occurred particularly in the steel industry in the United States. The principal reasons are lower cost and improved materials compatibility. This trend is expected to continue, but the fact remains that phosphate esters are inherently superior to poly esters in terms of fire resistance, hence are likely to maintain their position in market sector requiring a higher level of fire resistance. The market for fire resistant fluids is significantly driven by regulatory considerations, and today's trends could be either enforced or reversed by regulatory changes. Such changes might occur as the trend to create larger, harmonized economic markets between countries develops. Recently, two new tests have been developed to provide a fire resistance ranking system. These are the factory mutual spray flammability parameter and, in Europe, the Buxton test.

The development of niche market for new fire resistant synthetic fluids may also be noticed. Such fluids are unlikely to contain chlorine or bromine because of environmental considerations, which focuses attention on phosphorus containing fluids, where a relatively high level of fire resistance is required. Phosphazenes are a class of fluids that have some promise in this area, but their high cost is likely to lift their potential.

## **B. Turbine oils**

Heavy duty gas turbine designs are driven by the desire for higher efficiency, which means a trend towards higher gas temperatures. These developments are being made possible through the development and use of new heat resistant alloys and ceramics. As a result, the lubricant is exposed to increasingly higher temperatures, particularly in the central bearings and the exhaust end bearings. This will lead to use of synthetic lubricants with improved thermo-oxidative stability. Poly ( $\alpha$ -olefins) or PAOs and ester fluids are likely to find areas of application here. Gas turbines derived from aircraft turbines already use the same synthetic ester based lubricants as the jet engine, and this is likely to continue for the foreseeable future.

The development of steam turbines has been driven by the same desire for improved efficiency. As steam temperatures have raised, the need for synthetic fluids have developed. Most notably, the fire risk of mineral oils leaking onto steam lines at temperature well in excess of the auto ignition point of the oil has lead to the use of phosphate esters in the electro hydraulic turbine governor system. For example, a German report has indicated that 43% of fires in power stations originated in the lubrication system, and 49% from the hydraulic system, in the remainder, the source could not be identified. Thus, it is expected to see more advances in the use of fire resistant fluids in the lubrication system, particular in the environments where a fire could be devastating. Phosphate esters are the obvious candidates, and their use has been reviewed. The additional cost involved in the use of phosphate esters over a mineral oil in a new turbine adds very little to the total cost. This small price differential can be offset against the possibility of

a reduced capability, since the synthetic fluid has better air release properties. Additional saving may be realized through the possibility of reduced under floor fire protection and reduced fire insurance premiums. It also has been argued that mineral oil based turbine lubricants rely to some extent on regular topping up of the system with fresh oil to maintain performance. A reduction in top up rate coupled with generally higher temperatures could significantly reduce the life of mineral oil based lubricants and require the use of a synthetic fluid. PAO fluids or blend of PAOs with mineral oil would be favored for use. Longer term innovations to increase turbine efficiency include the use of ammonia/water mixtures, which also may require a new approach to lubrications.

### **C. Industrial gear oils**

The dominant trends in the lubrications of industrial gears are towards higher temperature, longer life, and lower friction these trends are a result of the designers' target of lower cost, simplified designs, and improved efficiency. More power through smaller gearboxes results in higher lubricant temperature. The longer life of a lubricant reduces maintenance cost and, in the limit of a "fill-for life" potential, there are considerable savings to be achieved from removing drain plugs and filler caps and simplifying design and manufacture. All these factors are leading to a gradual PROLOGUE of synthetic-based oils. In addition, the synthetic lubricants can offer significant advantages where very low temperatures are likely to be encountered. The leading candidate for use as the base stock for the synthetic gear oils is poly ( $\alpha$  olefins). When combined with the correct additive package, PAO based gear lubricants show much improved thermo-oxidative stability over mineral oil based lubricants. They also show a potential for reducing energy losses in the gear box. Frictional losses are reduced, as manifested by lower oil temperature in service. The lower oil temperature also helps increase service life. Poly glycols are reported to show particular advantages in worm gears, where relative motion of teeth is entirely sliding and frictional losses can be considerable. The use of the poly glycol reduces friction and lower operating temperature.

A minimum physical and performance specification for synthetic gear lubricants has been established by the American Gear Manufacturers' Association. However, the industrial gear lubricant market remains highly segmented, and further development of widely accepted gear oil classification is needed to allow ready definition of oil quality requirements. If such classifications can be developed, they can be expected to stimulate wider recognition and acceptance of synthetic industrial gear oils.

### **D. Compressor oils**

The compressor market can be split into three sectors. These are air compressors, compressors for other gases, and refrigeration compressors. Industrial air compressors make up the largest sector and have seen the successful utilization of synthetic based lubricants: the air compressors exposes the lubricant to air at high temperatures, which results in the ready oxidation of mineral based oils, necessitating frequent changing of a mineral oil based lubricant to allow continued operation of the compressor. The replacement of the mineral oil by a synthetic oil can greatly increase the time between lubricant changes, and the greater expense of the synthetic oil is more than offset by the reduction in the downtime and by the extended oil life. For example, in a rotary screw air compressor the time between oil changes can be

extended from 1000-2000 hours of operation to between 4000 and 8000 hours by replacing a mineral oil based lubricant with PAO based lubricant. In general, synthetic lubricants based on PAO or esters have enjoyed the most success.

Poly ( $\alpha$  olefins) has tended to find greater acceptance for use in rotary screw compressors, and esters have tended to be favored in reciprocating compressors. The reason for this is based on a perceived greater degree of lubricity from the ester based lubricant, which is beneficial in the prevention of wear between the piston and cylinder. However, the real world situation is more complex than is suggested by a simple comparison between the fundamental properties of esters type and PAOs, because in the finished air compressor lubricant there will also be chemical additives and associated carrier oils, and in the case of a largely PAO based lubricant there will almost certainly be between 5 to 15% of an ester component to ensure good seal swell characteristics, as well as to provide some improved lubricity and additives solubility. Because of flow maintenance costs, there is a trend to favor rotary screw compressors over reciprocating compressors. It is expected that the share of this market held by synthetic based lubricants will increase the desire for longer gain intervals will be desirable not only from an efficiency standpoint but also because of the increasing concerns with used oil disposal. In applications where biodegradability is a factor, poly ester based lubricants are expected to gain over PAO based lubricants. This might be accepted in the "mobile compressor" sector of the market, where spills and leakage into the environment are more likely.

Changes in the market for refrigeration compressor lubricants are driven by mandated changes in the refrigerant fluid used. This is most evident in the compressors used for automotive air conditioning and in the compressors found in domestic refrigerators and freezers. These compressor types traditionally have used the chlorofluorocarbon R-12 as the refrigerant fluid either mineral oil or alkyl benzene based lubricants. International agreements have mandated the phased replacement of chlorofluorocarbons with materials of lower ozone depletion potential. The R-12 in automotive air conditioning units and domestic refrigeration units has been replaced, mostly by the hydrofluorocarbon (HFC) R-134a, a much more polar molecule than R-12. For that reason it differs from R-12 in that it is not miscible with hydrocarbon based lubricants such as mineral oils, alkylbenzenes, or PAOs. Miscibility is an important requirement in the designs of these systems. Over the past 10 years, a considerable amount of work has been devoted to developing new lubricants for use with R-134a. Early work focused on polyalkylene glycol based lubricants followed by the development of suitable ester based lubricants. Initially these were of the polyolester type with R-134a miscibility governed by the length of the hydrocarbon chains. Malonate ester derivative was also developed which has very high miscibility with R-134a and can be blended with dibasic acid esters to make suitable lubricants for use in these R-134a compressors.

Other chemistries investigated have included derivatives of unsaturated PAO oligomers and fluorinated molecules, but to date these have not been successful for technical and economic reasons. The first generation lubricant for use with R-134a in automotive air conditioning units have been based on polyalkylene glycol. For domestic refrigerators, the lubricant of choice has been polyol ester based. The 1990s saw the development of this significant new market for the synthetic compressor oil, amounting to some 5000 tons of lubricant for automotive air conditioners and some 16000 tons of lubricant for R-134a compressors in domestic refrigerators and freezers each year.

In the industrial sector the refrigerant choice depends on the size of the system and the temperature range is needed. R-134a is used as a medium temperature refrigerant in conjunction with primary polyol esters. R-134a is borderline for use in freezers. Other refrigerants used are R-22 and other HFC blends with polyol esters primarily.

Another result of the phase-out of the CFCs is an increase in the use of ammonia based refrigeration systems. Ammonia based systems are primarily used in commercial applications, specifically secondary systems, which can be rigorously controlled to accommodate the toxic nature of ammonia. The secondary ammonia based system may be contained in a separate small building, where water is chilled by ammonia and then circulated throughout the main building for conditioning of the air. Adoption of the system also could result in increased use of synthetic lubricants, probably based on PAO, although hydro treated, highly paraffinic based lubricants are also likely to share a part of this market sector. Lubricants based on these lubricants show greater thermal stability with ammonia than do conventional oils. This set of properties result in reduced sludge and varnish formation, which allows extended drain interval. The PAO based lubricant has the advantage of superior low temperature fluidity. To increase the efficiency of the evaporating systems using ammonia efforts are underway to find a suitable soluble lubricant that will not coat the evaporator and hinder the efficiency. Mineral oils are insoluble in ammonia but some polyalkylene glycols have been found to be soluble and so their use may grow. Ester based lubricants are not suited for use with ammonia because of the excessive sludge formation associated with each lubricant.

For propane and other hydrocarbon refrigerants, polyglycols based lubricants have proved suitable. These fluids have the advantage of not dissolving the hydrocarbon and thus do not suffer from dilution and consequent loss of viscosity as do mineral oils.

In gas compressors, the nature of the gas determines the type of lubricant to be used. Certain polyglycols, as mentioned above, have the advantage of not dissolving hydrocarbons. This makes them particularly suitable for the lubrication of natural gas compressors. In addition, these polyglycols are toxicologically acceptable for use in low density polyethylene compressors. The use of the polyglycols based lubricant results in extended drain interval, reduced wear, and improved efficiency. However, the low density polyethylene market is mature and is expected to decline as a market for synthetic lubricants. New production is focused on linear low density polyethylene, which is a low pressure process that does not require the performance level of polyglycols lubricants. Either oxygen compressors are designed to run dry or, to minimize the risk of explosion, a low flammability lubricant, often a phosphate ester, are used.

#### **E. Paper mill oils**

Synthetic lubricants are beginning to establish niche positions in the pulp and paper industry. The key to their use is improvement in a plant's overall productivity. The industry typically will follow original equipment manufacturers' recommendations for the lubrication of new or revamped equipment. The trend is to run hotter, and newer machines tend to have smaller lubricant reservoirs. Synthetic lubricants offer greater ability than the currently used mineral oils, and their advantages are being recognized by OEMs, component manufacturers, and plant lubrication engineers. Poly ( $\alpha$  olefin) based lubricants are likely to take a significant position in coming years, particularly in drying and calendaring operations.

Synthetic greases also are developing niche application areas. For example, they are used in roller bearings in such areas as the wet end press section, where the combination of high loading, high temperature, and acidic conditions imposes a particularly severe operating environment. At the dry end, where dryer steam joints are equipped with roller bearings, synthetic based, lithium complex thickened greases find applications such as these is anticipated for a variety of synthetic and part synthetic lubricants. Where savings justify their use, even lubricants as expensive as perfluorinated polyether greases will find a niche.

#### **F. Industrial greases**

The need for greater appreciation of the lubrication of bearings has been highlighted. It was estimated that 43% of premature rolling bearing failures are due to improper lubrication- in many cases, the use of mineral oil grease in applications in which the performance limits of the material were exceeded. Synthetic industrial greases are thus finding increasing niche application areas as they offer increased service life under conditions of higher load and higher temperature. The benefit of using such greases is the potential for a significant reduction in maintenance and downtime. For the same reason there is a trend toward the use of sealed-for-life bearings. This trend also will develop the use of synthetic lubricants. Specialized synthetic lubricants also find niches in potentially hostile chemical environments, where superior stability constitutes as advantage. High performance lubricants of this type are unlikely to be biodegradable.

Biodegradable greases increasingly are being used in environmentally sensitive applications. For relatively simple applications, such biodegradable greases are likely to be based on vegetable oils, but more demanding applications will see the use of synthetic greases based on nontoxic, biodegradable synthetic esters.

#### **G. Metalworking oils**

Metalworking consumes a very large volume of fluids, many of which are based on water solutions emulsions. Since this industry, synthetic organic fluids have served largely as components in aqueous systems. Polyalkylene glycols find use, in aqueous solutions, in cutting oils and quenching oils. Long chain polyol esters and PAOs are finding increased use in steel and aluminum rolling oil formulations. The development of these uses has been and will continue to be driven by the desire for greater efficiency, higher quality, and ever increasing environmental pressures. These pressures already have had considerable impact in limiting the use of chlorinated materials, nitrites, and phenols in finished emulsion. The need to reduce smoke and mist formation in the workshop will require the use of increasingly stable and less volatile materials, a trend that will promote the continued development of synthetic organic fluids in formations.

#### **H. Food contacting oils**

Considerable quantities of oils are used in processes that bring them directly or indirectly into contact with food. The vast majority of these are white oils composed of mineral hydrocarbons refined sufficiently to be regarded as food grade. In the United States, fluids coming into contact with food require appropriate Food and Drug Administration (FDA) or U.S. Department of Agriculture (USDA) approval, but different regulations apply in different parts of the world. White mineral oils have come

under increasing scrutiny regarding their suitability for use where food contact is involved, and the results of a Shell study attracted much attention, particularly in Europe. However, further testing of white mineral oils did not fully substantiate these results, and such oils continue to be used in many food contacting applications. If however, white mineral oils are banned from significant sectors of this market, there will be considerable opportunities for alternate fluids. For many applications it is likely that vegetable oils could find a ready market; but in processes having a requirement for superior stability, it could prove necessary to use synthetic fluids. A prime example of this could be in the production of polystyrene. At the moment white mineral oil is used in the production of polystyrene as an integral lubricant and extender. Up to about 6% can be used, depending upon the polystyrene grade. In use, polystyrene goods come into contact with foods, and thus the mineral oil has to be of suitable food quality. In Europe, it is estimated that about 0000 tons of white mineral oil is consumed each year in this application. Vegetable oils are unlikely to be suitable for this application because the process temperatures are too high; hence there exists the possibility for development of a significant new market for suitably approved synthetic fluids. The situation offers a striking example of how toxicological concerns might result in new regulations having a significant impact on the fluids market. The outcome cannot be predicted at this time.

#### **I. Heat transfer fluids**

The heat transfer fluids market already has a substantial sector of synthetic fluids. For the world market, close to 20% of the annual volume of some 20 million gallons is synthetic fluid. In dollar terms, however, this \$100 million market is split such that half its value is derived from the synthetic fluids. Synthetics offer improved thermal stability and also improved low temperature characteristics over mineral oil based fluids. Even when the heat transfer function is concerned with high temperature only, better low temperature fluidity can prevent system shutdowns and the need to steam trace lines in cold ambient conditions. The types of synthetic fluid used have recently been reviewed, and their properties, temperature range of operation, and design parameters compared. General growth in this relatively mature market is expected to be at a few percent a year, with synthetics gradually increasing their share of the total market. New opportunities are presenting themselves in relatively lower temperature systems associated with the processes control of drug and specialty chemical production, and this sector of the market is predicted to show the fastest growth.

#### **J. Textile fluids**

The textile industry in developed countries continues to come under tremendous pressure from developing countries where labor costs are lower. To compete, the textile industry is responding through advanced technology to reduce the labor component of production, to increase production efficiency, and to produce superior quality goods. In addition, the industry is facing considerable environmental pressure in terms of workplace safety used in process oil formulations. However, these factors are having some impact on the fluids used in process oil formulations. However, this is an industry that is extremely cost conscious, and synthetic fluids will penetrate the mineral oil share of the market slowly and only to the extent that a clear cost performance benefits is realized.

In the production of texturized polyester and nylon yarns, greater efficiency is continuously sought through higher spinning and texturizing speeds and minimizing downtime of equipment needed for cleaning of hot plates and replacing of texturizing disks. The primary spin finishes applied after spinning and prior to texturizing today are largely synthetic based. Typically, these synthetic based finishes are applied as aqueous emulsion. Greater speed generally demands higher plate temperatures, and this requires the lubricant in the spin finish formulation to have higher thermal stability, or at least to decompose in a "clean" manner, leaving no deposits on the hot plate. Deposits on the hot plate impact on the heat transfer from plate to yarn and cause variability in quality in terms of texture and uniform dye ability. Variability in dye ability causes havoc in the production of first quality fabrics and cannot be tolerated. Deposits on the hot plate also can lead to increased filament leakage, which reduces efficiency. Filament breakage becomes a more serious problem as finer filament yarns are produced. Finer filament yarns are increasing their share of the market because of the generally superior aesthetics of fabrics and garment from such yarns. A higher smoke point is desirable to reduce contamination of the work place, and there is growing concern over the faith of used spin-finished lubricants in the environment. Synthetic lubricants, often esters, are used in these spin-finish formulations because their superior thermal stability and higher smoke points make their use cost-effective versus mineral or vegetable oils.

Many other process oils used in the textile industry, such as coning oils, are largely mineral oil based. This is because the temperatures melt in downstream processing are such lower than those found on texturizing hot plates, and the cost-effectiveness of synthetic fluids is more difficult to demonstrate. Only as regulatory action demands it will be seen as a major switch away from these mineral oil based systems. However, there will continue to be situations in which synthetic-based oil will solve particular problems and the use of the more expensive product will be justified. In particular, certain synthetic fluids have higher smoke points than mineral oils, and their attractive feature will become more important. Synthetic fluids are found in ring spinning and twisting. The benefits are seen largely in increase efficiency through less down-time and lower energy consumption. In particular, synthetics can be used to replace grease on solid rings and they have the added benefit of cleaning petroleum-fouled rings and maintaining clean rings almost indefinitely.

Specialty yarns are a small but established market for synthetic fluids. A higher price of such yarns means that a more expensive fluid can be tolerated as long as its superior performance justifies its use. Synthetic fluids, silicons in particular, find application in the lubrication for spandex yarns. As the demand for such yarns increases, we can expect to see a corresponding increase in the quality of synthetic fluid consume. Silicon also finds application in the lubrication of polyester staple yarns used as the stuffing in pillows, quilts and duvets. This is because the particular friction characteristics of silicon oils have proved to be most suitable in maintaining the bulking characteristics of the staple. Such applications will continue to be developed as niche opportunities for the synthetic fluids.

### **K. Drilling mud fluids**

Drilling muds were traditionally water based, and today much development effort still goes into improving their qualities and performance. Indeed, one of the objectives of such development activity is the replacement of oil based muds, which earlier displaced water based muds in severe drilling environments such as those found in the North Sea. The more robust oil based muds allowed for much

more efficient drilling, reducing drilling time by 30% or more. Unfortunately, oil based muds have proved to be unacceptable environmentally, particularly in the sea. In the North Sea, this has resulted in ever tightening regulations governing oil based muds and the quality of mud allowed to be discharged along with cuttings into the sea. This has proved the stimulus for development of muds based on synthetic fluids that will prove environmentally acceptable. The first example of such a fluid is the ester around which Baroid developed its "Petro free" mud. This product is vegetable oil based, specifically palm oil. Other fluids introduced into this market are the ether based fluids from Anchor and PAO based fluids from M.I. Drilling.

Certain linear  $\alpha$  olefin fluids are also suitable for use in drilling fluids. The principal characteristics of these fluids are a high degree of biodegradability and low toxicity toward aquatic species. Baroid supports its claim by describing biodegradation tests in seawater under both aquatic and anaerobic conditions. The PAOs that find application are typically dimmers of decene with limited chain branching. Other fluids that have been considered are detergent alkylates and food grade paraffins. Their use was experimental and their long term use is not thought to be viable.

The market for drilling mud fluids is still developing, and the final key for success will depend on the regulations imposed by the governing authorities. However, we believe that the fundamental drive for environmentally improved muds will continue to represent a significant opportunity for synthetic fluids tailored to provide the right balance of properties. The higher cost of synthetic based fluids against water based fluids is being offset by higher drill rates and longer bit runs. The potential market is several tens of thousands of tons a year, which is very sizable by the standards of today's markets for synthetic fluids.

#### **L. Electro-rheological Fluids and Ferro fluids**

When considerable future industrial fluid trends, it is appropriate to review the potential for the development of systems utilizing "smart" materials, which have the ability to perform both sensing and actuating functions. Two examples are electro rheological fluids and ferrofluids.

Electro rheological fluids have been known for more than 50 years, but the last 14 years they have seen resurgence in research and development activity in the creation of such fluids and their potential applications. The near instantaneous response of an electro rheological fluid to an applied electric field is potentially a very attractive property in the design of systems that will respond to take advantage of the high speed with which a computer can detect, manipulate, and respond to and take advantage of high speed with which a computer can detect, manipulate, and respond to signals. Added to this, such fluids offer the prospect of simplified design and fewer moving parts, which lead to greater reliability at lower cost. The development of anhydrous systems gives the promise of extending the temperature range over which such fluids can operate. It is clear that some of the projections made in the mid to late 1980s for commercial application of this technology and its subsequent growth of systems depending on them, could create a substantial market; if these develop, however, industrial applications will follow.

If electro rheological fluids do become commercially significant, they will represent a substantial potential market for synthetic fluids. Certainly, electro rheological fluids can be produced using many different fluids, including mineral and vegetable oils, as the continuous phase, but we believe that it is



likely that a potentially commercial fluid will require careful control of the properties of the continuous and dispersed phases. The fact that a synthetic fluid can be made to very precise quality control limits will favor its selection and use.

Ferrofluids react to changing magnetic fields, becoming more viscous as the magnetic field strength increases. They are made by suspending ferromagnetic particles in an appropriate liquid medium. Synthetic fluids designed to have the correct balance of properties find use in this not believe that large volumes of synthetic fluids will be used in such specialized applications in the foreseeable future.

# CHAPTER 4

## Economic Analysis

### I. PROLOGUE

Market Overview: Inherent Benefits Driving the Growth of Synthetic Lubricants: Thanks to their underlying advantages, synthetic lubricants are gaining increasing acceptance in the United States. Besides high viscosity indexes, synthetic oils have higher flash points, lower pour points, and very low volatility. These make them valuable blending components when compounding for extreme service at both high and low temperatures. Further, they can be constructed accordingly for high-performance applications that require excellent heat control, wear resistance, and energy efficiency. The uniform molecular weight of synthetic lubricants maintains their integrity.

However, rising crude prices are causing a surge in the prices of raw materials used for producing synthetic lubricants, affecting margins for manufacturers. As a result, leading companies are expanding their capacity, integrating vertically, or acquiring competitors in the market. 'Synthetic lubricants are also facing stiff competition from mineral oil-based lubricants and a new type of base stock called Gas to Liquid (GTL),' notes the analyst of this research service. 'GTL lubricants are completely saturated, less volatile, devoid of nitrogen, sulphur, and aromatics, and cheaper than synthetic lubricants.

### II. POLY ( $\alpha$ -OLEFIN) MARKET EXPECTATION

The Polyalphaolefin (PAO) segment is expected to have a high growth rate when compared to other synthetic lubricant base stock markets. The key drivers for PAO include extended drain intervals and better reliability and consistency. The drain interval of PAO is superior to that of Group I, Group II, Group III, and GTL, making it a preferred lubricant base stock. PAOs' drain intervals are usually measured in years. This factor is expected to play a major role in automotive engine and gear oils, and all the other specialty oils. The shift from mineral oil and other

lubricants to PAO-based synthetic lubricants is also expected to catalyze the growth rate of PAO base stocks in the future.

'Overall, the U.S. synthetic lubricant base stocks market was worth \$901.2 million in 2007,' says the analyst. 'Aided by the growth of PAOs and Polyalkylene Glycols (PAGs), the market is expected to grow at a compound annual growth rate (CAGR) of 5.2 percent in the future.'

In spite of relatively low growth rate in the overall market of lube oil and a current market of only 1.8% of this market by synlubes, they are experiencing a higher growth rates due to technology upgrades in the automotive and industrial sectors. As this report shows, the synlubes market is estimated to rise from the present global volume of 0.74 million metric tons per annum to 1.1 million metric tons in 2003 and 1.78 in 2008. The dollar value of these in markets is 2.23, 3.96 and 7.32 billion respectively in 1998, 2003, and 2008. Their share of the overall global lube oil market is thus projected to grow from the present level of 1.8% to 2.5% in 2003 and 3.7% b the year 2008.

### **III. COST ESTIMATION:**

Whether it is business situation or a day-to-day event in somebody's personal life, there are large numbers of economic decision making involved. One can manage many of these decision problems by using simple economic analysis. Certain factors which are involved for this analysis are as follows;

- Price of the raw material
- Transportation cost of the raw material (it is assumed that the price of raw material is location dependent)
- Availability of the raw material
- Quality of the raw material

Apart from these there are certain other factors which are also involved in these, they can be:

- Maintenance cost
- Labour cost
- Operating cost

Consider the alternative of sourcing raw materials from a nearby place with the following characteristics:

- The raw material is more costly in the nearby area.
- The availability of the raw material is not sufficient enough to support the operation of the industry throughout the year.

- The raw material requires pre processing before it is used in the production process. This would certainly add cost to the product.
- The cost of transportation is minimal under this alternative.

On the other hand, consider another alternative of sourcing the raw material from a far off place with the following characteristics:

- The raw material is costly at the far off place.
- The cost of transportation is very high.
- The availability of the raw material at the site is abundant and it can support the plant throughout the year.
- The raw material from the site does not require any pre-processing before using it for production.

Under such a situation, the procurement of the raw material should be decided in such a way that the overall cost is minimized.

#### **IV. ELEMENTS OF COST:**

Cost can be broadly classified into variable cost and overhead cost. Variable cost varies with the volume of production of production while overhead cost is fixed, irrespective of the production volume.

Variable cost can be further classified into direct material cost, direct labour cost, and direct expenses. The overhead cost can be classified into factory overhead, administration overhead, selling overhead, and distribution overhead.

Direct material costs are those costs of material that are used to produce the product. Direct labour cost is the amount of wages paid to the direct labour involved in the production activities. Direct expenses are those expenses that vary in relation to the production volume, other than the direct material costs and direct labour costs.

Overhead cost is the aggregate of indirect material costs, indirect labour costs and indirect expenses. Administration overhead includes all the costs that are incurred in administration the business. Selling overhead is the total expenses that are incurred in the promotional activities and the expenses relating to sales force. Distribution overhead is the total cost of shipping the items from the factory site to the customer site.

## **V. MATERIAL SELECTION FOR A PRODUCT/SUBSTITUTION OF RAW MATERIAL:**

The cost of a product can be reduced greatly by substitution of the raw material. Among various elements of cost, raw material cost is most significant and it forms a major portion of the total cost of any product. So, any attempt to find a suitable raw material will bring a reduction in the total cost in any one or combinations of the following ways:

- Cheaper raw material price
- Reduced machining/process time
- Enhanced durability of the product

### **Maintenance:**

Maintenance can be classified into two types: Preventive maintenance and Breakdown maintenance.

#### **Preventive maintenance (PM):**

It is the periodical inspection and service activities which are aimed to detect potential failures and perform minor adjustments or repairs which will prevent major operating problems in future.

#### **Breakdown maintenance (BM):**

It is the repair which is generally done after the equipment has attained down state. It is often of an emergency nature which will have associated penalty in terms of expediting cost of maintenance and down time cost of equipment.

Preventive maintenance will reduce such cost up to a point. Beyond that point, the cost of preventive maintenance will be more when compared to the breakdown maintenance cost. The total cost, which is the combination of preventive and breakdown maintenance cost, will go on decreasing with an increase in the level of maintenance up to a point. Beyond that point, the total cost will start increasing. The level of maintenance corresponding to the minimum total cost is the optimal level of maintenance.

## VI. DERIVATIONS

### 1) Steady State Continuous Stirred Tank Reactor (CSTR):

(Input of A to the reactor (moles/time)) = (output of A from the reactor (moles/time)) + (disappearance of A by reaction within the reactor (moles/time)) + (accumulation of A within the reactor (moles/time))

Since steady state, accumulation = 0

Input of A to the reactor (moles/time) = output of A the reactor (moles/time) + disappearance of A by reaction within the reactor (moles/time)

$F_{A0}$  = molar feed rate of A to the reactor in moles/time

$V$  = Volume of the reactor

$C_{A0}$  = molar concentration of A in stream entering the reactor in moles/volume

$V_0$  = volumetric feed rate

We have,

$$F_{A0} = C_{A0} * v_0$$

Molar feed rate of A to the reactor =  $F_{A0}$

The molar feed rate at which A is reacting in the reactor =  $F_{A0} X_{A0}$

$F_{A0} X_{A0}$  = (moles A fed/time)\* (moles A reacted/moles A fed)

Moles A reacted/time =  $F_{A0} * X_{A0}$

Molar flow rate of A leaving the reactor =  $F_A$

(molar flow rate at which A is fed to the reactor)- (molar rate at which A is consumed in reactor)  
= (molar rate at which A leaves the reactor)

$$F_{A0} - F_{A0} X_{A0} = F_A$$

Output of A from reactor in moles/time =  $F_A = F_{A0} (1-X_A)$

Rate of disappearance of A by reaction within the reactor in moles/time =  $(-r_A)V$

Now we get,

$$F_{A0} = F_{A0} (1 - X_A) + (-r_A)V$$

$$F_{A0} X_{A0} = (-r_A)V$$

Rearranging,

$$C_{Af} = C_A$$

$$V/F_{A0} = X_A / (-r_A)$$

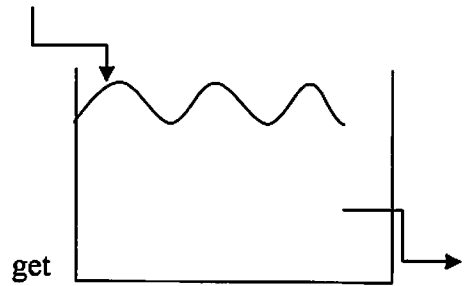
$$V/F_{A0} = \tau / C_{A0} = X_A / (-r_A)$$

$$\tau = 1/s = V/v_0 = V C_{A0} / F_{A0} = X_A C_{A0} / (-r_A)$$

we

$C_{A0}, v_0$

$F_{A0}, X_{A0}$



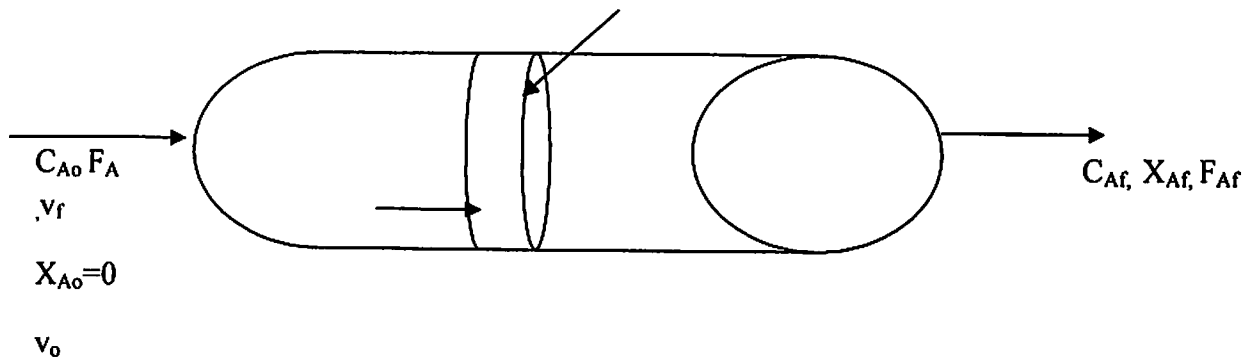
**Figure 13** - CSTR

When  $X_A$  and  $(-r_A)$  are evaluated at the exit (stream) conditions, which are the same (i.e. identical) as the conditions prevailing within the reactor (e.g., composition, temperature – the exit composition from the reactor is identical to the composition within the reactor).

The above derived equation is the performance equation for a CSTR applicable for any value of  $\square_A$ .

## 2) Steady State Plug- Flow Reactor (PFR):-

**Figure 14** - PFR



Input of A, moles/time =  $F_A$

Output of A, moles/time =  $F_A + d F_A$

Rate of disappearance of A by reaction, moles/time =  $(-r_A) dV$

$$= (\text{moles A reacting}/(\text{time}) (\text{volume of fluid}) * (\text{volume of element}))$$

$$F_A = F_A + d F_A + (-r_A) dV$$

We know,  $F_A = F_{A0} (1 - X_A)$

$$d F_A = d [ F_{A0} (1 - X_A) ] = -F_{A0} .dX_A$$

$$F_A = F_A + d F_A + (-r_A) dV$$

$$F_A = F_A - F_{A0} .dX_A + (-r_A) dV$$

$$F_{A0} .dX_A = (-r_A) dV$$

The above equation is the differential form of the performance/ design equation for a plug flow reactor (-applicable for the differential section of reactor volume  $dv$ ). For the reactor as a whole, this equation must be integrated (after separating the variables).  $F_{A0}$  in the above equation is constant, but  $(-r_A)$  depends upon the concentration or conversion.

So rearranging the terms accordingly, we get  $dX_A / (-r_A)$

$$\int_0^V dV / F_{A0} = \int_0^{X_{Af}} dX_A / (-r_A)$$

$$V / F_{A0} = \int_0^{X_{Af}} dX_A / (-r_A)$$

$$V = F_{A0} \int_0^{X_{Af}} dX_A / (-r_A)$$

$$V / F_{A0} = \tau / C_{A0} = \int_0^{X_{Af}} dX_A / (-r_A)$$

Or,  $\tau = V / v_0 = V C_{A0} / F_{A0} = \int_0^{X_{Af}} dX_A / (-r_A)$ , for any  $\square_A$

The above derived equation is the performance equation for a plug flow reactor for any  $\square_A$ .



## VII. COST ESTIMATION FOR THE REACTOR USED IN THE PRODUCTION OF PAO:-

Timms, IChemE (1988) gave a simple equation for capital cost estimation; updated to 1998:

$$C = 9000 * N * Q^{0.615}$$

Where

C = capital cost in units (Rupees)

N = Number of functional units

Q = plant capacity, tons per year

In US dollars

$$C' = 14000 * N * Q^{0.615}$$

Where C' = capital cost in US dollars

Number of units for processing of PAO in this project = 5

Units- 1 Mixer, 1 Reactor, 2 Separators and 1 Condenser

Using the above given formulae –

$$N = 5$$

Plant Capacity, Q = 10000 liter

C = Rs. 12978141.76 or nearly Rs. 13 million

C' = \$ 20188220.52 or nearly \$ 20.2 million

### Lang factors -

The factorial method of cost estimation is often attributed to Lang (1948). The fixed capital cost of the project is given as a function of the total purchase equipment cost by the equation:

$$C_f = f_L * C_e$$

Where

C<sub>f</sub> = fixed capital cost,

C<sub>e</sub> = the total delivered cost of all the major equipment items: storage tanks, reaction vessels, columns, heat exchangers, etc.,

f<sub>L</sub> = the "Lang factor", which depends on the type of process.

f<sub>L</sub> = 3.1 for predominantly solids processing plant

f<sub>L</sub> = 4.7 for predominantly fluids processing plant

f<sub>L</sub> = 3.6 for a mixed fluids-solids processing plant

The values given above should be used as a guide; the factor is best derived from an organization's own cost files.

Above equation can be used to make a quick estimate of capital cost in the early stages of project design, when the preliminary flow-sheets have been drawn up and the main items of equipment roughly sized.

Item

Process type- Fluids

1. Major equipment, total purchase cost

PCE (Process Equipment cost)

f1 Equipment erection	0.4
f2 Piping	0.70
f3 Instrumentation	0.20
f4 Electrical	0.10
f5 Buildings, process	0.15
*f6 Utilities	0.50
*f7 Storages	0.15
*f8 Site development	0.05
*f9 Ancillary buildings	0.15
TOTAL=	2.4

2. Total Physical Plant Cost (PPC)

$$PPC = PPE * (1 + f1 + f2 + f3 + f4 + f5 + f6 + f7 + f8 + f9)$$

$$\text{Or, } PPC = PPE * 3.4$$

f10 Design and Engineering	0.30
f11 Contractor's fee	0.05
f12 Contingency	0.10
TOTAL=	0.45

$$\text{Fixed Capital} = PPC * (1 + f10 + f11 + f12)$$

$$\text{Or, Fixed Capital} = PPC * 1.45$$

(\*Omitted for minor extensions or additions to existing sites.)

Fixed capital calculations:-

Taking C = PPE;

From calculations-

$$PPC = \text{Rs. } 44125682$$

$$\text{Fixed capital} = \text{Rs. } 63982238.9 \text{ or Rs. } 64 \text{ million (nearly)}$$

Annual production cost calculations:-

Fixed cost-

1. Maintenance cost, M = 5 to 10 per cent of fixed capital

Taking maintenance cost as 10%, hence

$$M = 10\% \text{ of Rs. } 63982238.9$$

$$\text{Or, } M = \text{Rs. } 6398223.89 \text{ or Rs. } 6.4 \text{ million (nearly)}$$

2. Operating labour cost, L -

If the plant works 24 hours a day in 3 shifts of workers, 5 members each shift, for the annual working days of 300 days (60 days needed for cleaning, repairs etc.) with a wage of Rs. 20 per hour then,

$$L = 3(\text{shifts}) * 5(\text{members}) * 20(\text{Rs. /hour}) * 24(\text{hours}) * 300(\text{days})$$

$$L = \text{Rs. } 2160000 \text{ or Rs. } 2.16 \text{ million}$$

3. Laboratory costs, LC = 20 to 23 per cent of operating labour cost

Taking LC = 20 % of operating labour cost

$$LC = \text{Rs. } 432000 \text{ or Rs. } 0.432 \text{ million}$$

4. Supervision cost, S = 20 per cent of operating labour cost

Hence, S = Rs. 432000 or Rs. 0.432 million

5. Plant overheads cost, P = 50 per cent of operating labour cost

Hence, P = Rs. 1080000 or Rs. 1.08 million

6. Capital charges, C = 10 per cent of the fixed capital

Hence, C = Rs. 6398223.89 or Rs. 6.4 million (nearly)

7. Insurance cost, I = 1 per cent of the fixed capital

Hence, I = Rs. 639822.389 or Rs. 0.64 million (nearly)

8. Local taxes, LT = 2 per cent of the fixed capital

Hence, LT = Rs. 1279644.778 or Rs. 1.3 million (nearly)

9. Royalties, R = 1 per cent of the fixed capital

Hence, R = Rs. 639822.389 or Rs. 0.64 million (nearly)

Variable cost-

1) Raw materials cost, RM-

Taking ethylene feed rate as 20 kg per minute and its cost = Rs. 0.46 per kg

$$\text{Hence RM} = 20(\text{kg/minute}) * 60(\text{minutes}) * 24(\text{hours}) * 300(\text{days})$$

$$\text{Or, RM} = \text{Rs. } 3974400 \text{ or Rs. } 3.9744 \text{ million}$$

2) Miscellaneous materials, MM = 10 per cent of maintenance cost

Hence MM = Rs. 639822.389 or Rs. 0.64 million (nearly)

3) Utilities cost-

a) Electricity cost, E- taking cost as 1.0p/MJ (Rs.1=100p) and units used per year = 120000MJ

$$E = \text{Rs. } 1200$$

b) Cooling water cost, CW- taking cost as 1.5 p/t (1 t = 1000 kg) and total units used = 120000 t

$$\text{Hence, CW} = \text{Rs. } 1800$$

4) Shipping and packaging - usually negligible

Annual production cost = Fixed costs + Variable cost

Or, Annual production cost = (M+L+LC+S+P+C+I+LT+R) + (RM+MM+E+CW)

Hence, Annual production cost = Rs. 24076959.73 or Rs. 24.08 million (nearly)

$$\text{Production Cost} \left( \frac{\text{Rs.}}{\text{kg}} \right) = \frac{\text{Annual Production Cost}}{\text{Annual Production Rate}}$$

Hence production cost = 24076959.73 / 10000 = Rs. 2407.695973 or Rs. 2400 (nearly)

### VIII. DETERMINATION OF REACTOR DIAMETER AND VOLUME

Data assumptions:-

Volumetric flow rate,  $V_0 = 20$  liter/minute

Rate constant,  $K = 0.3$

Height/length of the reactor = 30 m

Used relations:-

$$\text{Volume} = \text{Area} * \text{Height}$$

$$V = \Pi * r^2 * h$$

$$r = \sqrt{\frac{V}{\Pi * h}}$$

CSTR relation -

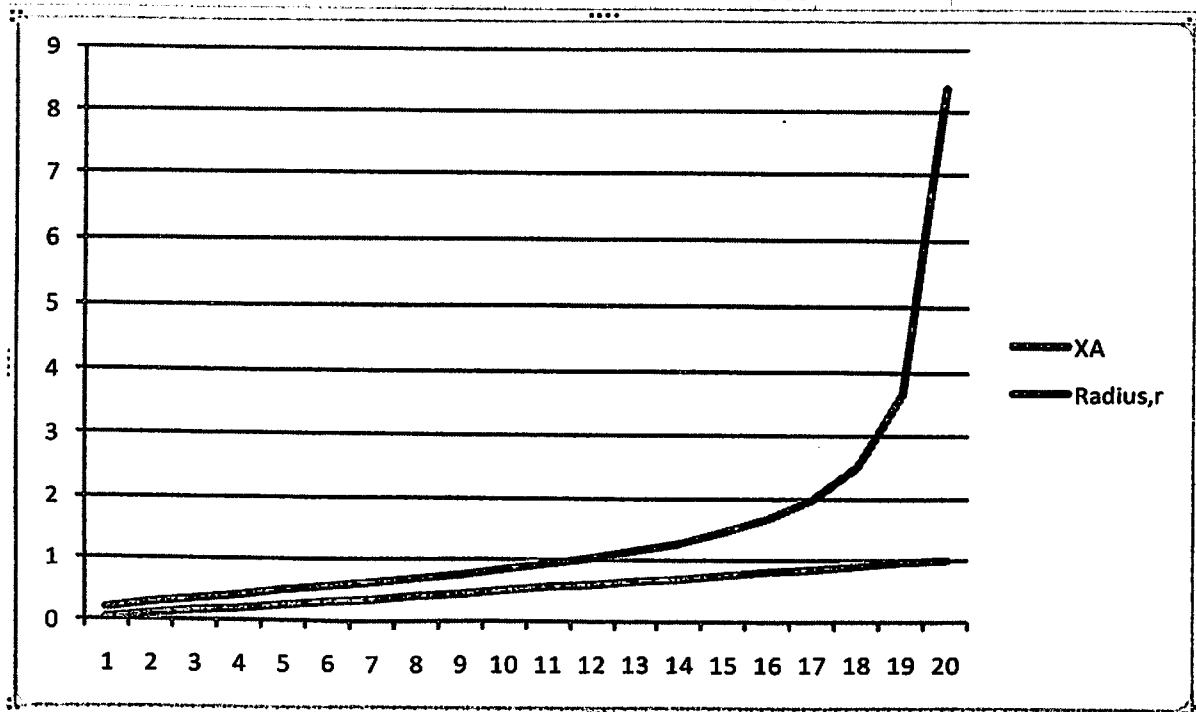
$$\frac{V}{V_0} = \frac{Xa}{K(1-Xa)}$$

PFR relation -

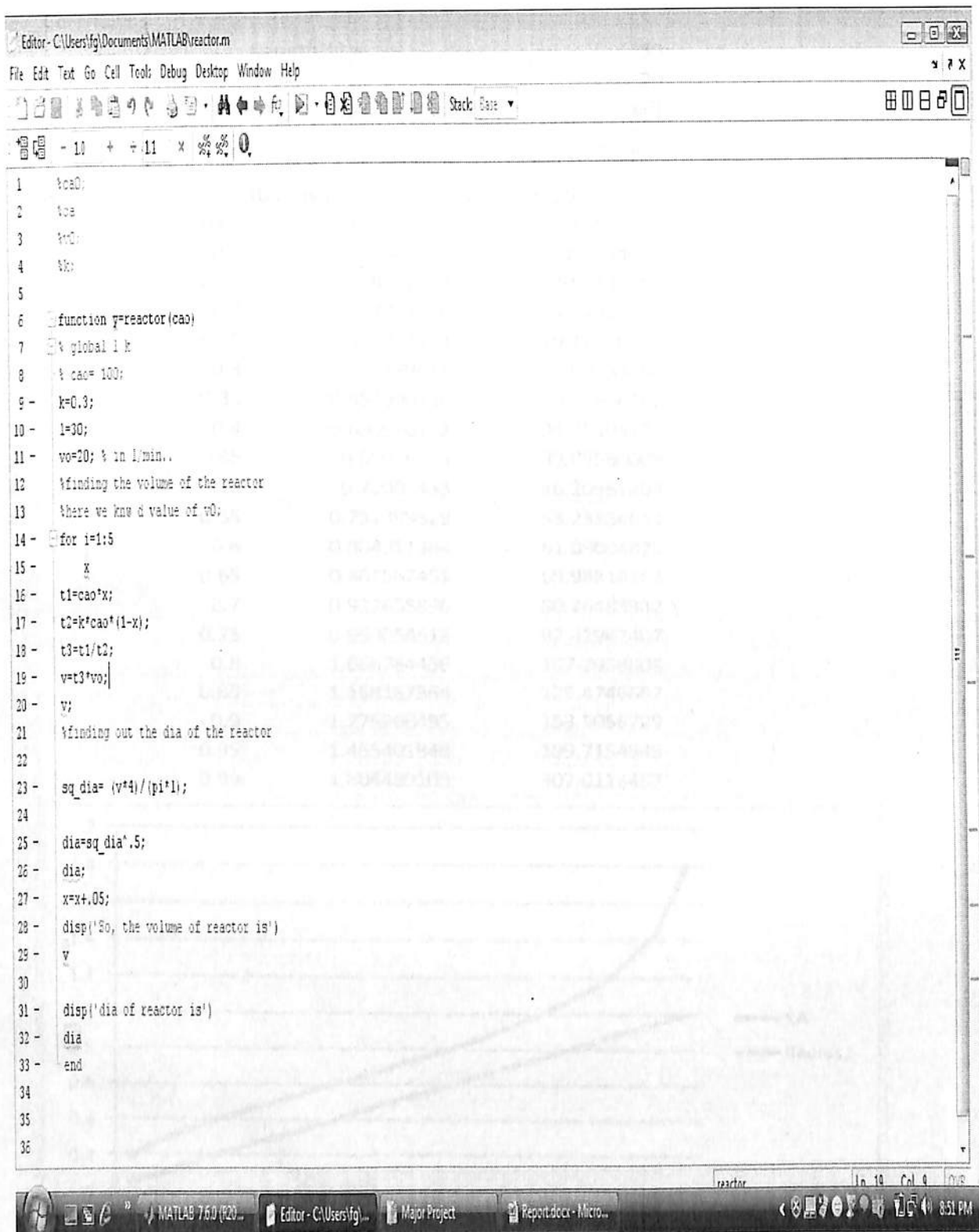
$$\frac{V}{V_0} = \frac{\ln(1-Xa)}{K}$$

**A) Variation of radius(r) w.r.t. changes in XA for CSTR**

XA	Radius,r	Voulume, V
0.05	0.192909947	3.50877193
0.1	0.280291655	7.407407407
0.15	0.35323814	11.76470588
0.2	0.420437483	16.66666667
0.25	0.485479388	22.22222222
0.3	0.550481883	28.57142857
0.35	0.617033533	35.8974359
0.4	0.686571534	44.44444444
0.45	0.760600024	54.54545455
0.5	0.840874966	66.66666667
0.55	0.929622252	81.48148148
0.6	1.029857302	100
0.65	1.145919419	123.8095238
0.7	1.284457727	155.5555556
0.75	1.456438163	200
0.8	1.681749931	266.6666667
0.85	2.001682795	377.7777778
0.9	2.522624897	600
0.95	3.665288999	1266.666667
0.99	8.366600269	6600



For doing the same calculations in MATLAB the program needed will be:-



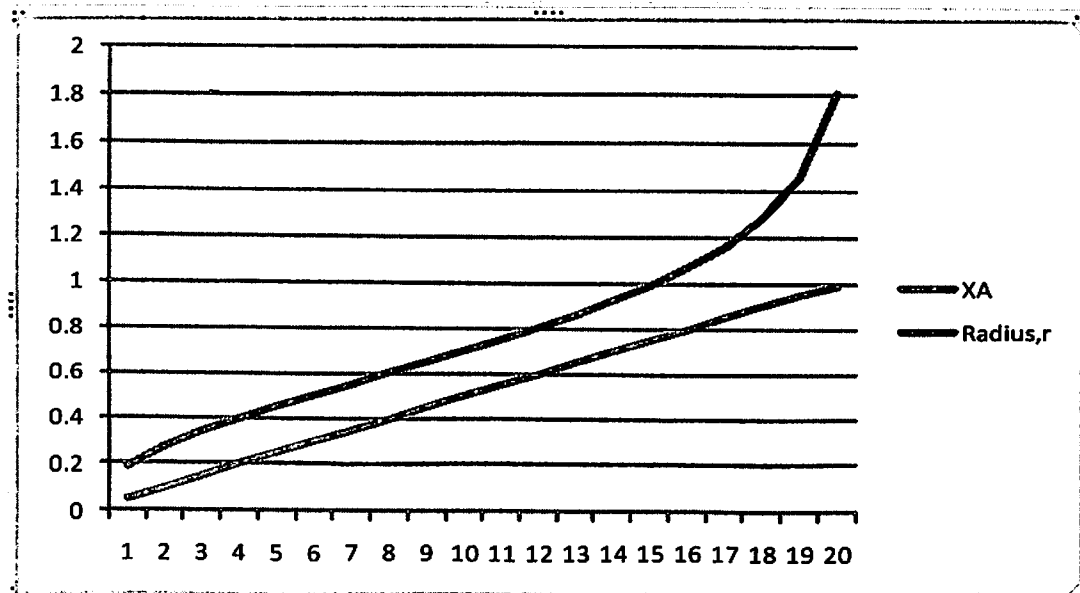
```
1 %cao;
2 %k;
3 %t0;
4 %v;
5
6 function y=reactor(cao)
7 % global i k
8 % cao=100;
9 k=0.3;
10 i=30;
11 wo=20; % in l/min.
12 %finding the volume of the reactor
13 %here we know d value of t0;
14 for i=1:5
15     x
16     t1=cao*x;
17     t2=k*cao*(1-x);
18     t3=t1/t2;
19     v=t3*wo;
20     y;
21 %finding out the dia of the reactor
22
23     sq_dia= (v*4)/(pi*i);
24
25     dia=sq_dia*.5;
26     dia;
27     x=x+.05;
28     disp('So, the volume of reactor is')
29     y
30
31     disp('dia of reactor is')
32     dia
33     end
34
35
36
```

**B) Variation of radius(r) w.r.t. changes in XA for PFR**

Constant :-

Length(L) = 30  
 Vo = 20  
 K = 0.3

XA	Radius, r	Volume, V
0.05	0.190441555	3.419552959
0.1	0.272941998	7.024034377
0.15	0.338987278	10.8345953
0.2	0.397213128	14.87623675
0.25	0.451011714	19.17880483
0.3	0.502189611	23.7783296
0.35	0.551900336	28.71886107
0.4	0.600990712	34.05504158
0.45	0.65016385	39.85580005
0.5	0.70007433	46.20981204
0.55	0.751399629	53.23384641
0.6	0.804911384	61.08604879
0.65	0.861567451	69.98814163
0.7	0.922655896	80.26485362
0.75	0.990054612	92.41962407
0.8	1.066764456	107.2958608
0.85	1.158187364	126.4746657
0.9	1.275966485	153.5056729
0.95	1.455401848	199.7154849
0.99	1.804489108	307.0113457



As seen from the calculations it can be seen that the CSTR is more preferable for  $XA=0.8$  since a lesser value of  $XA$  gives a lesser value of radius but at the expense of the conversion rate ( $XA$ ) itself. On the other hand, in this case since value of radius is lower hence reactor cost will be also lower. However an increase in value of  $XA$  above 0.8 needs an exponentially greater value of radius of the reactor making  $XA=0.8$  more feasible to use economically.

On the basis of the calculations earlier done, PFR is likely to be selected for reactor design. However since the reaction is polymerization reaction in nature hence in PFR corrosion problem is enormous which affects the economic value making the PFR reactor costly and less considerable. Thus it can be concluded that economically CSTR is more viable.

## **IX. COMPARISON BETWEEN SYNTHETIC AND CONVENTIONAL FUEL OILS**

An economic analysis assuming synthetic oil lasts three times as long as conventional oil is presented below for a 12-quart capacity vehicle. Oil and filter disposal information was based on estimates from the San Antonio Air Logistics Center. Lubricant and filter price information was provided by the vendors.

### **Assumptions:**

- 30 vehicles in fleet.
- Labour cost: \$20/hr.
- Labour: 0.5 hour per oil change.
- Oil disposal: oils are recycled at no cost to the facility.
- Oil cost: Synthetic - \$14.51/gallon, Conventional - \$4.42/gal.
- Conventional oil is changed three times per year; synthetic oil is changed once per year.
- Filters cost \$6.00 each.
- Filter disposal: estimated at \$100 per drum, 100 filter per drum
- Oil capacity of vehicle is an average of 12 quarts (or 3 gallons).



## Annual Operating Cost Comparison for Synthetic Oil verses Conventional Oil Use

Table 28 -

<b>Operational Costs</b>	<b><u>Synthetic</u></b>	<b><u>Conventional</u></b>
Labour:	\$300	\$900
Oil Costs:	\$1,305	\$1,193
Filter Cost:	\$180	\$540
Filter Disposal:	\$30	\$90
<b>Total Costs:</b>	<b>\$1,816</b>	<b>\$2,723</b>
<b>Total Income:</b>	<b>\$0</b>	<b>\$0</b>
<b>Annual Benefit</b>	<b>-\$1,816</b>	<b>-\$2,723</b>

### Economic Analysis Summary:

- Annual Savings for Synthetic Oils: \$908
- Capital Cost for Diversion Equipment/Process: \$0
- Payback Period for Investment in Equipment/Process: Immediate

# CHAPTER 5

## Commercial Developments

### 1) PROLOGUE

In the last 10 years synthetic lubricants have transitioned from being a niche segment of some industrial application to a mainstream of the whole lubricant industry. The first commercially used synthetic lubricants were silicones, developed by Dow Corning and General Electric in 1943. It was followed by polyalkylene glycols in 1945, developed by Union Carbide, diesters in 1951, phosphate esters in 1953 and polyol esters in 1963.

Amsoil Corporation introduced the first API rated fully synthetic engine oil in 1972, although Agrip had launched a part synthetic motor oil, Sint 2000, in Italy in 1969, Mobil 1 was launched as the first worldwide fully synthetic engine oil in 1977.

Synthetic lubricants are now used in over 70 different application sectors. Although its high prices was formerly considered as a barrier for its widespread applications, it is now more generally accepted that the synthetic lubricants provide outweighed benefits primarily because of its properties and its widespread usage. Hence it has been predicted that the demand for the mineral based lubricant oil will remain static, the demand for synthetic lubricants is supposed to rise at 5 to 7 % per year rate. This inevitably means that the demand for mineral oil based lubricants is likely to fall over the next 5-10 years.

According to some industry analysts synthetic lubricants are forecasted for more than 5% of the total lubricants market in 2000. However by 1997, synthetic and VHVI-based lubricants already accounted for slightly more than 10% of the European lubricants market, almost 3% of the North American lubricants market, and around 2 % of the lubricants market in other regions of the world. Total worldwide demand for synthetic and VHVI based lubricants amounted to over 1.2 million tons in 1997.

## II) ECONOMIC COMPARISON OF SYNTHETIC LUBRICANTS

### A. Advantages and disadvantages of different synthetic oils

Each synthetic lubricant/oil has its own good and bad points, some better others worse in comparison. In general the synthetic lubricants are highly desirable because of their following properties:-

- Good inherent lubrication properties
- Good low temperature properties
- Good high temperature properties
- Good viscosity/temperature properties
- Low volatility
- Good stability
- Low toxicity

In some applications, an apparent inferior performance might turn out to be a positive advantage. Some examples can be cited:

The incompatibility of some polyalkylene glycols with mineral hydrocarbon enables the former to be used in natural gas compressors.

The thermal depolymerization of polyisobutenes (PIBs) enables them to be used in clean burning two stroke oils.

The chemical structure of diesters that gives them poor hydrolytic stability also means that these compounds are readily biodegradable.

The most important consideration in assessing comparative advantages and disadvantages is this: if a specific application does not require a particular performance property, then synthetic oil that performs well in that respect will not have any added value for that application. Conversely, if the synthetic oil performs poorly, it will not matter for that application.

### B. Balancing conflicting performance requirements

The lubrication chemist's task in formulating a cost effective lubricant to perform a specific function is not easy. In many cases, a large number of performance requirements, some of which may conflict will need to be satisfied. There are a number of such examples where conflicting properties are favorable such as:

Blending a diester with a PAO to improve the latter's seal swell properties in automotive engine oil tests is likely to detract from the excellent hydrolytic stability characteristics.

Polyisobutenes are very shear stable and can be used to make very good gear oils, but low temperature properties make them unsuitable for use in outdoor gearboxes in cold climates.

Using viscosity index improvers in conventional mineral oils can be a cheap way to enhance the viscosity/temperature properties, but at the expense of overall shear stability properties.

Many experienced users have shown that the task of formulating a finished lubricant is analogous to producing a perfectly round inflated balloon; if pushed in any small bump on one part of the balloon it produces another bump on the other side, and if the push is excessive then the overall product might not be a desired one.

### C. Costs and cost comparisons

The 1997 costs of mineral and synthetic base oils of various types are listed in the following table, which also lists their relative costs compared with 150 solvent neutral (150 SN) high viscosity index base oil. The following is the European list prices for lubricant base oils:

**Table 29 -**

<b>Fluid</b>	<b>List price (\$/ton)</b>	<b>Price relative to 150 SN</b>
150 SN mineral oil	235	1.0
500 SN mineral oil	235	1.0
Brightstock	300	1.3
VHVI mineral oils	700-900	2.9-3.4
XHVI mineral oils	1000-1200	4.3-4.7
Poly( $\alpha$ -olefins)	1450-1550	6.2-6.6
Polyalkylene glycols	2000-2200	8.5-9.4
Polybutenes	950-1750	4.0-7.5
Diesters	1900-3500	8.1-14.9
Polyol esters	11900-3600	8.1-15.3
Phosphate esters	3500-4500	14.9-19.2
Alkylbenzenes	1250-1350	5.3-5.7

However these comparisons can be highly misleading as for many applications mineral oil require large quantities of additives to bring their performance to a satisfactory level. This adds significantly to the total cost, secondly a number of other costs need to be considered when one is attempting to compare performance. These include the following:

**Immediate costs**

Base oils

Additives and components

Formulation

Laboratory testing

Rig and specification testing

Field trials

Blending and storage

Transportation

Sales

**Hidden costs**

Distribution

Handling and preparation

Monitoring

Servicing

Collection

Disposal

Marketing

A more realistic comparison of cost with regard to performance would focus on the price paid by the user. Although this depends on all factors identified as above, it is likely to be a more accurate guide to comparative performance. In these terms, the most readily obtainable price comparisons are those for retail motor oils sold at the pump and in do-it-yourself shops.

**III) DEVELOPMENTS IN THE SYNTHETIC LUBRICANTS BUSINESS**

The synthetic lubricants business has been progressing steadily since the late 1970s and early 1980s, when chemical companies became interested in the commercial potential of specialty products that could command high prices of bulk chemical feedstock such as ethylene, propylene, and naphtha, which in turn are linked to the price of crude oil and natural gas.

It was an unfortunate coincidence that shortage of chemical feedstock occurred in 1987 and 1988, pushing ethylene and some derivatives prices to very high levels and bulk poly ( $\alpha$ -olefins) to nearly \$2000/ton. As a result of pricing swings, the price ratio of PAOs to mineral base oils, for example, has been varied between 3.5:1 and 7.0:1 during the 1990s. The lesson has been that the lubricants industry needs to understand the driving forces in synthetic lubricant production and pricing, while the chemical industry needs to understand the economics of the base oil industry, which has remained linked to crude pricing for 30 years. Only the VHVI oils have been able to break this pattern.

Automotive lubricants have seen by far the biggest increase in synthetic fluid use in the 1990s. Increased sales of part synthetic oils led to significant increase in demand for both PAOs and diesters from lubricants blenders. Sales of VHVI oils are booming. The pattern started in Europe in the late 1980s, and spread to all regions of the world, as lubricant marketers recognized the commercial gains possible from a "good/better/best" range of automotive engine oils.

Although synthetics have been for many years in the industrial markets, steady growth is still being experienced for PAOs, PIBs, PAGs and long chain polyol esters, particularly in compressors, bearings, gears, and circulation systems, and for fire resistance hydraulics and metalworking applications. Esters are emerging as the dominant technology for biodegradable lubricants, as used in forestry, waterways, and construction. Phosphate esters are making a comeback against polyol esters in fire resistant hydraulic fluids, but the long term position of polyglycols in brake fluids is uncertain, with the PROLOGUE of DOT 4 fluids, which meet specifications of the U.S. Department of transportation.

Technical understanding of the properties of synthetic lubricants has been increasing for some years. Some applications have been lost by one synthetic, but gained by another. Where demonstrable advantages can be assessed (e.g., in high performance compressors), there is a solid acceptance at all levels, from OEMs, lubricant companies, and customers. This is the key to success. If any of the three elements of consensus is missing, there is only disappointment and frustration. The market penetration of synthetic fluids received a major boost in the 1980s from the PROLOGUE of the NOACK volatility test and is now receiving a second boost from biodegradability and toxicity issues, generally summarized as environmental benefits.

Consolidation and focus also have begun to emerge in the synthetic lubricants business. Hacto purchased the industrial synthetic lubricants business of Huls, including the Anderol, PQ, and Aosyn brand names, in September 1996. The company then purchased Royal lubricants, the aviation and military lubricants business of Shell Oil, in November 1996. Hacto, which has manufactured and marketed ester fluids for many years, announced that it will operate its synthetic industrial lubricants business under the Anderol brand and its aviation and military synthetic lubricants business under the Royal brand, for foreseeable future.

Amoco chemicals purchased the PAO business of Albemarle Corporation in January 1996. Albemarle had decided to focus on its core  $\alpha$ -olefins business, while Amoco had recognized that PAOs would be a strategic fit with its lubricants business. In the early 1990s, no oil company that manufactured VHVI oils had a chemical division that made PAOs or esters, while no chemical company that manufactured PAOs or esters was owned by an oil company that made VHVI base oils. By the end of 1997, this situation had begun to change radically. Now, Mobil Oil makes VHVI base oils and Mobil Chemical makes PAOs, as do Neste Oil/Neste Chemical and Chevron Oil/Chevron Chemical. Uniroyal chemical also announced a progressive 50 % increase in its high viscosity PAO manufacturing capacity in July 1996, in response to increasing market demand.

The performance advantages of synthetic lubricants are becoming understood and accepted by the market, and synthetic fluids are becoming integrated into the strategic business plans of the majority of lubricants manufacturers and marketers. These are significant commercial advances from the situation only a decade ago, and trend is unlikely to atop now.

# CHAPTER 6

## Instrumentation and control

### I. PROLOGUE – (STORAGE TANKS)

Storage tanks should be of welded steel construction. Underground storage tanks are not recommended because of the difficulty of locating leaks. Nonetheless, some states require underground storage tanks. Diking, drainage, and tank supports should be blue printed to conform to local regulations. A rule of thumb commonly practised for determining the size of storage facilities suggests that storage facilities be 1½ times the size of shipments received. The secondary containment requirements as well as tank layout and spacing requirements should be in accordance with NFPA 30. Rotating equipment such as pumps should be kept outside of the secondary containment area. Some facilities may require larger inventories, and thus storage facilities, because of seasonal transportation troubles.

The storage tank inlet should be located at the bottom of the tank. Should a top inlet be hoped, the fill pipe should be extended to a depth no greater than the diameter of the fill pipe from the bottom of the tank to minimize static charge accumulating during filling. The fill pipe should be connected electrically to both the tank flange and the transfer pipeline. The purpose of this electrical connection is to dissipate any static charge which may build up during filling.

PAO and dimer storage tanks are kept under a nitrogen-blanketed atmosphere (10 in. H<sub>2</sub>O). A nitrogen blanketing system is necessary in applications where the product is going to be stored for long periods of time and peroxides/carbonyls would present a trouble in the process. A nitrogen system betters a positive pressure and adds nitrogen as the product is withdrawn and the tank breathes. This prevents the PROLOGUE of air that can cause peroxide buildup in the product and keeps moisture from condensing in the tank. Free water will settle out in the bottom of the tank and will normally not be seen until the tank is stripped. Dissolved water up to the saturation level may be found in products. If water is a critical contaminant, the PAO or dimer sample should be tested periodically and free water withdrawn through the sump.



All product storage tanks should have combination pressure relief/vacuum breaker valves. The combination pressure relief/vacuum breakers are blue printed to relieve to atmosphere to prevent over-pressuring as well as to open to atmosphere to protect against damage from low pressures (vacuum).

All of the lines and valves, as well as the tank, can be carbon steel. Nonetheless, carbon steel lines will accumulate rust if allowed to remain empty for long periods of time. In this situation the first few gallons of product moved down the line may have a yellow to orange color and may contain particulates depending on the amount of rust that has accumulated.

Unlined carbon steel tanks may also accumulate rust above the liquid level. This rust, along with the condensate, will settle to the bottom of the tank and may not be seen until the tank is stripped. Rust can be avoided by having storage tanks lined with zinc, epoxy, or another coating that is compatible with these products.

Specific bulk storage blue prints must conform to insurance underwriter's codes and local fire and building regulations. Critical blue prints, placement, installation, and maintenance requirements are usually addressed in these codes and regulations and must be followed.

Inspect tanks periodically for leaks and service in accordance with API Standard 653.

Workers should never be permitted to enter an empty tank which has been practised for poly( $\alpha$ -olefin) products until the requirements of the OSHA Permit-required Confined Space Standard (29 CFR 1910.146) and the Safe Entry Recommendation of API Standard 2015 have been met, including, but not limited to, required concentrations for oxygen.

## **II. PARTICULATE MATTER**

PAO and dimer products should be free of particulate matter when shipped. Nonetheless, some particulate matter may originate from outside contamination via the receiving-transfer system.

Particulate matter may be avoided by:

1. Paying careful attention to cleanliness.
2. Filtering product to remove particulate matter before use.

## **III. FILTERS**

Since small amounts of foreign matter may enter storage tanks and transport vessels from various sources, a filter in the transfer piping between the storage tanks and processing equipment is recommended. This can be accomplished by inserting a corrugated cellulose filter paper (5  $\mu$ m)

inside a woven polyester fiber (10  $\mu\text{m}$  mesh) cartridge-type filter. Chevron Phillips Chemical Company uses a 2  $\mu\text{m}$  filter paper in a steel case housing. Former types of product compatible filters might also be practised. Flow rates and pressures should be practised to determine the proper filter for specific situations. Inspect and renew filter cartridges periodically.

#### **IV. HOSES**

Hard piping is preferred to the use of hoses where possible and practical. If hoses are needed for loading or unloading operations, they should be inspected and pressure tested at the intervals required by the various regulations. The preferred type hose would be a steel braided hose.

#### **V. PUMPS**

Liquid product can be transferred by pump or vacuum. For most product handling operations, centrifugal pumps with mechanical seals perform satisfactorily. The pump manufacturer can recommend the proper type of pump if the following parameters are known:

1. Flow, in gallons per minute,
2. Size and length of suction and discharge lines,
3. Suction and discharge pressures, and
4. Range of product temperatures during transfer.

A drain valve should be installed at the lowest point in the system so that the pump and all piping can be completely drained and washed before any maintenance work is done. Totally enclosed fan-cooled (TEFC) motors are recommended. Nonetheless, local fire and insurance codes should be consulted to determine if an explosion-proof motor must be practised. Pump seals must be capable of meeting EPA emission standards - this requires tandem or double seals. Tandem seals enhance safety when pumping these products (at elevated temperatures). Demisting systems should be practised to keep pump bearings lubed.

#### **VI. VALVES**

Full-bore ball valves are preferred for pigged pipelines. Gate valves, butterfly valves, or ball valves may be practised for pipelines that are not pigged. These valves should be made of cast iron, case steel, or former recommended materials. Valves should be packed with the following graphite materials:

1. Garlock EVSP Simplified (#9000/98)
2. Garlock70# / 98 (-400 to 1200 oF , 10,000 psi)
3. Garlock1303 (good for steam)
4. Slade 3300G (-400 to 1200 oF , 10,000 psi)

Most effective packing is a flexible die-form ring with flexible braided end-rings, practised for field repacking.

## VII. PIPELINES

The following are recommended practices in engineering pipelines for PAO products:

1. A minimum of flanged connections should be practised to avoid potential leaks.
2. Lines should not be buried because of the difficulty of checking for leakage.
3. All lines should be sloped with drain valves at appropriate locations so that they can be completely drained for maintenance.
4. All newly installed pipelines should be pressure tested by an approved method before use.
5. Bellows valves for 2-inch and smaller lines are recommended to eliminate emissions from packing glands.

## VIII. FIRE INFORMATION

### a. Fire Hazards:

PAO are not considered to be flammable or combustible or highly responsive. Nonetheless, despite their low flammability ratings, they will burn at high temperatures. They do respond with strong oxidizing agents, such as peroxides, nitrates, and chlorates.

### b. Fire Fighting Instructions and Combustion Products:

For fires involving this material, do not enter any enclosed or confined fire space without proper protective equipment, including self-contained breathing apparatus to protect against products of combustion or oxygen deficiency. Normal combustion forms carbon dioxide and water vapor, while incomplete combustion may develop carbon monoxide.

Fires involving PAO can be safely extinguished with carbon dioxide (CO<sub>2</sub>), dry chemical, and foam and water fog. If electrical equipment, such as motors, open hot plates, or open electrical switches, is involved, the foam should be practised with caution.

Drainage and runoff should be controlled and collected in a remote location for recovery or disposal. Minimize spread to reduce cleanup price.

## **IX. PERSONAL PROTECTIVE EQUIPMENT & OCCUPATIONAL EXPOSURE LIMITS**

### **Personal Protective Equipment:**

Consider the potential hazards of this material, applicable exposure limits, job activities, and former substances in the work place when blue printing engineering controls and selecting personal protective equipment. If engineering controls or work practices are not adequate to prevent exposure to harmful levels of this material, the personal protective equipment listed below is recommended. The user should read and understand all instructions and limitations supplied with the equipment since protection is usually provided for a limited time or under certain circumstances.

No special skin protection is usually needed. No protective clothing is normally required. Nonetheless, wearing protective clothing can minimize skin contact. No eye protection is normally required. No respiratory protection is normally required. If user operations generate an oil mist, determine if airborne concentrations are below the recommended mineral oil mist exposure limits. If not, wear a NIOSH approved respirator that provides adequate protection from measured concentrations of this material.

## **X. DISPOSAL**

PAO products are not intentionally disposed of in quantity because of their commercial value. Waste oil should be taken to a certified waste oil collector who then gives the waste oil to a registered refiner to recycle. Off-specification material may possibly be recycled or practised as a fuel.

For approved disposal methods of contaminated PAO, local health and environmental authorities must be contacted. Contaminated materials have to be placed in disposable containers. The containers must then be disposed of in compliance with the applicable regulations.

# CHAPTER 7

## Environmental Impact

### I) PROLOGUE

In 1985 nearly 4.5 million tons of lubricants was used in the European community. Of this, some 2.5 million tons was consumed in service leaving 2.0 million tons of waste oil. Out of this 0.7 million tons was reused as a fuel supplement, 0.7 million tons was recycled, 0.6 million tons was unaccounted for. This has however changed with time, i.e. with the raised concerns for the environment the energy sector has also raised its standards and there is a greater concern for the fate of uncollected waste.

To properly address the overall potential environmental impact of a chemical it is necessary to analyze the life cycle of the material which includes its energy output, wastes, reuse, and recycle capabilities. This analysis is also commonly known as the "Cradle to grave" or life cycle analysis.

To further check upon the chemical impact there are a number of regulatory bodies in various countries such as TSCA in USA, CEPA in Canada, PICCS in Philippines, etc. Toxic potential of a particular chemical is evaluated depending upon the amount of exposure magnitude and the intrinsic toxicity of the material itself. Besides these bioaccumulation and biodegradability are also important factors in determining the environmental impact of the environment. Bioaccumulation can be defined as the increase in the concentration of the chemical with time and it depends on factors such as degree of uptake, distribution, metabolism, etc. Biodegradability can be understood as the rate with which the chemical undergoes chemical breakdown to its simpler forms. This method can be abiotic as well as biotic, including hydrolysis, photosynthesis and biodegradation. In order to assess lubricant biodegradability the following tests are conducted worldwide-

Test name	Test method
CEC test	CEC-L-33-A-93
Modified AFNOR test	OECD 301A
Modified MITI test	OECD 301C
Closed bottle test	OECD 301D
Modified OECD screening test	OECD 301E
Zahn wellens test	OECD 302B
Modified sturm test	OECD 301B
EPA shake flask test	
Gledhill shake flask test	Modified U.S. EPA shake flask test
ISO test	ISO 9439:1990

These tests do not necessarily give the same result for a particular chemical because of the differences in their methodology. Some lubricant types and their ranges of biodegradability is as given –

**Table 31 -**

Lubricant type	Range of biodegradability as evaluated by the CEC-L-33-A-93 test (21 days)(%)
Hydrocracked	25-80
White oils	25-45
Mineral oils	10-45
Brighstock	05-15
Vegetable oils	75-100
Poly( $\alpha$ -olefins)	20-80
Alkylbenzenes	05-25
Diesters	50-100
Polyols	05-100
Aromatic esters	00-95
Polypropylene glycols	10-30
Polyethylene glycols	10-70

Other synthetic lubricants show similar effects. Branched alkylbenzenes have lower biodegradabilities than linear alkylbenzenes. PAGs based on ethylene oxide are more biodegradable than those based on propylene oxide. Biodegradability also decreases with increasing saturation as shown by the following example:

Dimerate ester = 50% biodegradability

Hydrogenated dimerate ester = 25% biodegradability

## II) POLY ( $\alpha$ -OLEFINS)

PAOs are not expected to create acute or chronic toxicity to humans if exposure occurs by the dermal, oral, or inhalation routes. In addition, they are not expected to cause skin or eye irritation. This toxicological evaluation is based on the very limited toxicity data available on the PAOs are tests of acute toxicity including oral LD<sub>50</sub>, skin and eye irritation tests, inhalation LC<sub>50</sub>, and tests for comedogenicity (chlorance formation potential).

Although only little information is available on aquatic toxicity of PAOs, they are not expected to be toxic to aquatic organisms. Also even though they have high solubility in liquids, they do not bioaccumulate in general because of their properties. The water solubility component seems to impose a cutoff point beyond which compounds are not sufficiently soluble to be toxic. The physicochemical characteristics of PAOs (i.e., low water solubility) seem to place them beyond this cutoff point in water solubility, which renders them inert in aquatic systems.

Low viscosity PAOs (i.e. 2 & 4 cst) can be classified as relatively biodegradable in aqueous systems as defined by the CEC L-33-T-82 test (Amoco Corporation data). However, this does not mean that PAOs are biodegradable. In water, PAOs may adsorb organic particulates or form colloidal suspensions, thereby decreasing the available surface area for bacterial biodegradation. The inability of bacteria to interact with the hydrocarbon substrate would produce very little apparent biodegradation as defined by currently accepted protocols, such as the closed bottle test for ready biodegradability.

Therefore, in general, owing to their low aqueous solubility, PAOs should be relatively inert in aquatic systems in regards to acute toxicity, biodegradability, and bioaccumulation.

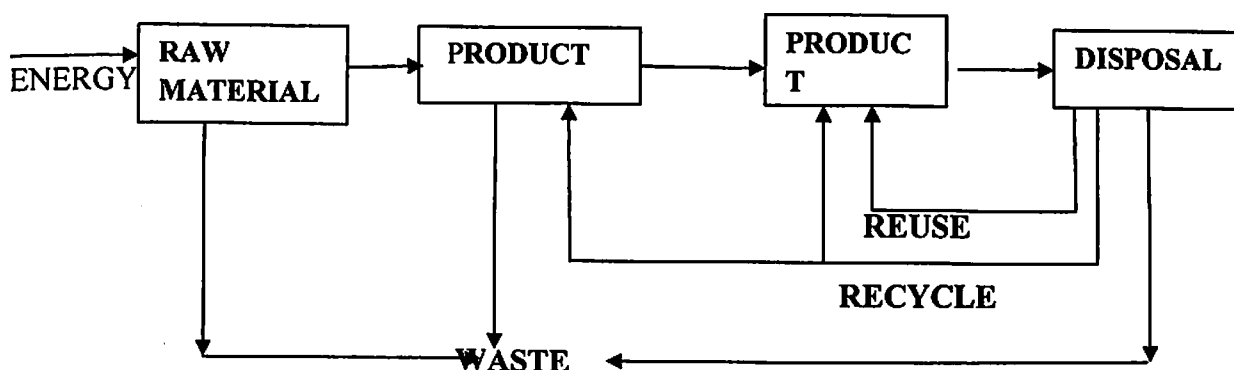


Figure 15 - Schematic diagram for a "CRADLE-TO-GRAVE" analysis

### III) ENVIRONMENTAL LABELING –

Environmental labeling schemes (i.e. ecolabeling) are being developed and instituted by governments worldwide to help increase consumer awareness of environmental issues and to aid people in selecting products that are environmentally compatible. It is anticipated that future market trends will be significantly impacted by consumer demands for environmentally sound products. Ecolabelling programs now in place are as follows:-

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European union	EEC ecolabeling scheme
Germany	Blue angel
Nordic countries	White swan
Canada	Environmental choice program
Japan	Ecomark
United states	Green cross and green seal

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### IV) **HEALTH, ENVIRONMENT, FIRE, AND ACCIDENTAL RELEASE INFORMATION**

All grades of PAO are synthetic base oils (not refined petroleum base stocks). The promising of these base oils (that are prepared by this process) to cause cancer has not been specially addressed by the OSHA Hazard Communication Standard 29 CFR 1910.1200, the International Agency for Research on Cancer (IARC), nor the National Toxicology Program (NTP) Annual Report. Based on the outcomes from mutagen city tests, process conditions, and chemical analysis, these oils are not anticipated to cause cancer.

#### HEALTH HAZARDS AND FIRST AID

**EYE CONTACT:** This substance is not expected to cause long-drawn-out or significant eye irritation.

First Aid: No first aid routines are required. As a preventative measure, remove contact lenses if worn and flush eyes with water.



**SKIN CONTACT:** This substance is not anticipated to cause long-drawn-out or significant skin irritation. Not anticipated to be harmful to internal organs if absorbed through the skin. Long-drawn-out and frequent skin contact with this material should be avoided as a good safety procedure.

First Aid: No first aid routines are required, but as a preventative measure the skin should be washed thoroughly with soap and water. The contaminated clothes should be removed and washed.

**INGESTION:** Since PAO 2 CST, PAO 2.5 CST, and PAO 4 CST (Types of PAOs) as well as C10 Dimer and C12 Dimer, have low viscosities, these materials can enter directly into the lungs if swallowed or if subsequently vomited; they are difficult to remove once in the lungs and can cause serious injury or death.

First Aid: If swallowed, do not provoke vomiting. Give the person a glass of water or milk and then acquire immediate medical attention. If the person is unconscious, do not give them something to drink, but obtain appropriate medical attention immediately.

**INHALATION:** This substance may cause respiratory irritation or former pulmonary effects following long-drawn-out or repeated inhalation of oil mist at airborne levels above the recommended mineral oil mist exposure limit (ACGIH TLV = 5 mg/m<sup>3</sup>; STEL = 10 mg/m<sup>3</sup>). Synthetic fluid PAO 2 CST and 2.5 CST may be toxic if inhaled as an oil mist.

First Aid: Individuals exposed to unreasonable levels of oil mist in the air should be moved to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention if coughing or respiratory discomfort happens.

## V) ECOTOXICITY/ENVIRONMENTAL FATE

**ECOTOXICITY:** Based on outcomes of laboratory tests with rainbow trout, daphnia, and freshwater algae, PAO's are not anticipated to be harmful to aquatic organisms. PAO's are not anticipated to bioaccumulate.

**ENVIRONMENTAL FATE:** PAO's are not considered to be swiftly biodegradable, but some products are inherently biodegradable based on standard biodegradation tests. Nonetheless, they are expected to completely biodegrade over extended periods of time.

## **CONCLUSION & RECOMMENDATION:-**

Mineral oils cannot meet all requirements for frictional contacts imposed by applications as lubricants or as operational fluids. As a result, certain synthetic fluids have gained significant importance. These fluids can be classified either by production process, composition, or chemical structure. An overall comparison with reference to mineral oils shows that synthetic fluids are superior to mineral oils only in certain properties. To obtain a practical overall comparison, therefore, weighing factors must be applied to the special properties of fluids

Considering all the parameters of the economics like cost of construction, maintenance cost, operating cost, we come to the conclusion that the reactor of **diameter size 3.35 m** and **height of 30 m** is a good choice for the formation of PAO from the ethylene as a feedstock by the polymerization reaction. The cost of ethylene also indicates that it is one of the good feedstock for the PAO formation. We know that higher the area of the reactor more the conversion will take place as the contact area increases, but considering to the economical parameters the higher area leads to the higher maintenance cost as well as increase in the cost of construction. The reactor design includes the design at constant **height** which we took as **30 m**, whereas, the conversion was varied. Based upon the reactor design we calculated the radius as well as the volume of the reactor, we suggest the reactor of **diameter 3.35 m** and the height is best suitable reactor as the percentage conversion is also good which will make our requirements of production and also economical in the terms of different types of cost in economics.

On comparison of plug flow reactor with the Continuous Stirrer Reactor we observe the cost of construction as well as the maintenance cost is less for the Continuous Stirrer Reactor. Though the conversion of the ethylene is more in case of the plug flow reactor, but due to the cost and other factors like Operating conditions, Operating Cost, Maintenance Cost, Quality yield we recommend the process should be carried out in the Continuous Stirrer Reactor.

Therefore based on our study we conclude that the **CSTR with volume (266 m<sup>3</sup>)** and the **diameter (3.35 m)** and the **height of 30 m** is best suitable for the process of the formation of PAO from the ethylene by the polymerization reaction.

Apart from the cost estimation PAO possesses many of the properties which is best to handle according to the use, i.e., automotive field, Aerospace and many such fields. The properties which distinguish it from other synthetic fluids and also these are green lubes for automotive sector, military field.

Synthetic lubricants are replacing the conventional lubricants like mineral oils and other such fluids in use for the industries fast. Hence a lot of consideration has to be given to the

synthetic fluids that have possible future utilization. Thus, based on the factors which PAO have it is very much acceptable, worthy, and of course a healthy decision to choose PAO as a futuristic fuel for various purposes.

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