A REVIEW OF CURRENT FUELS, FUEL CHEMISTRY, AND FUEL TRENDS

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INTRODUCTION

Current light duty and heavy duty engine fuels include a wide range of alternative, petroleum and synthesized fuels. Current trends in research on fuels include biodiesel, catalytically reformed fuels, alcohol and synthesized fuel supplements. Major factors affecting the fuel trends include the supply and demand for petroleum, environmental concerns, government regulations, consumer satisfaction and economics. Regulations around the world are established that tighten emissions regulations and impact global fuel compositions. In addition, growing global environmental concerns have lead to demands for more environmentally friendly hydraulic fluids and other lubricants. Minimizing the environmental impact of fuels and lubricants continues to be a challenge for OEM's, additive, and lubricant manufacturers.

Current research on fuels includes a variety of synthetic fuels derived from petroleum by-products, natural gas, coal, and natural resources. Studies have shown that the use of alternative fuels also requires consideration of the lubricants and tribology of the engine. Studies have shown that methanol, ethanol, and M-85 can cause lubricant related problems. Deterioration of lubricant additive packages exposed to the fuels reduces the performance properties of the lubricant. Removal of sulfur from diesel fuels resulted in engine problems related to the tribology of the system components and changes in the physical characteristics of the fuel. The separation of additive packages can be fuel selective and corrected through formulation changes in the lubricants.

This review will consider some of the types of fuels, their origin or processing, some advantages and disadvantages of the fuels. The current availability and the future trends related to fuels, lubricants, and environ-mental issues will be discussed. The types of fuels and their origin will be reviewed. Then, the processing and chemistry of the fuels will be briefly discussed and the trends and the possible scenarios affecting the trends will be summarized.

TYPES OF FUELS. A list of today's fuels and the primary source of the fuels are found on Figure 1.

PETROLEUM:	**NATURAL GAS:**
GASOLINE	METHANE
DIESEL FUEL	LPG
AVIATION FUELS	MeOH
COAL:	**AGRICULTURE:**
METHANE	MeOH (WOOD)
GASOLINE (SASOL)	EtOH (CORN)
METHANOL (MeOH)	BIODIESEL
SHALEOIL&TAR SANDS: OIL PRODUCTS	

FIG.1 - FUELS AND SOURCES

The major sources of the current fuels are fossil fuels made from petroleum and coal. Trends on energy consumption and sector usage are well documented in the literature [1-3] and will not be covered in detail. However, the industrialized world is now consuming over 130 Quads of oil per year, about half of the total amount of crude produced. The developing countries consumed only about 20% of the total but their consumption has increased by a factor of 4 over the past thirty years. At this rate of consumption our finite supply of oil may last another 50 years.

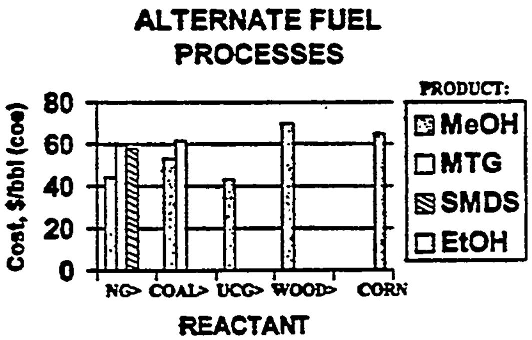


FIG. 2 - CRUDE OIL EQUIVALENT $

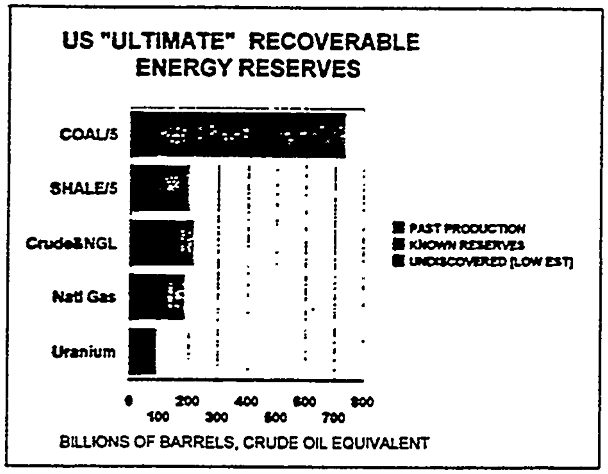


FIG.3 - U.S. OIL RESERVES (1980)

In 1992, the U.S. used about 17 million bbl/day [2]. The amount of petroleum used by various sectors in the US in 1992 ranges from over 60% for the transportation sector to about 3% for the electric utilities. Residential use was 7.6 % and industrial use was 27.9%. Comparing all energy sources, transportation used some 40% compared to 25% for industry. In comparison, Japan uses 50% for industry and a little over 20% for transportation. Considering third world countries, India uses about 55 % for industry and about 25% for transportation. In China about 65% of all energy consumed is used for industry and less than 5% is used for transportation.

There is also a discrepancy in how efficiently we use energy. China is one of the least efficient users of energy because of its dependence on coal and relatively ineffective technology. However, China's energy efficiency is improving rapidly. China has also started to exploit some of its large petroleum re-serves in the South China Sea as well as on the mainland. An interesting comparison is that of energy intensity or the amount of energy it takes different countries to produce US$1 of gross domestic product (GDP). UN researchers found the Japanese industry used only 5 megajoules to produce US$1 of GDP while the US required 12 megajoules. China used 66, India used 33, and Mexico 23 megajoules.

In 1992, the U.S. consumed more than one-quarter of the world's petroleum consumption [2]. Imports accounted for 46.1% of this use. Yet the cost of gasoline in the U.S. remains lower than it was in 1989. The current cost of a barrel of crude oil is around $17 dollars per barrel (1990 Dollars), a drop of $3 from 1990.

This makes the economics for most of the alternative fuels unacceptable and unlikely to make significant gains, unless other factors are involved. The price per barrel of crude needs to be over $40 per barrel for most alternative fuels to be competitive, Figure 2. In 1981, cost predictions were as high as $80/bbl by the year 1985 [4]. This was based on the oil crisis crude prices. The cost of crude increased from $3/bbl to $32/bbl from 1973 to 1980.

ORIGINS OF THE BIG THREE

When considering energy sources, petroleum, natural gas, and coal are the big three energy sources. The 1980 U.S. estimate of the reserves for these energy sources are shown on Figure 3. Two obvious observations are that there are considerably more coal and shale reserves in the world than any other source, billions of crude equivalent barrels and the amount remaining is less than the reserves remaining. Natural gas and petroleum are about equivalent. We have continued to find new sources of petroleum and the 25 year estimate in 1980 is now 25 to 50 years.

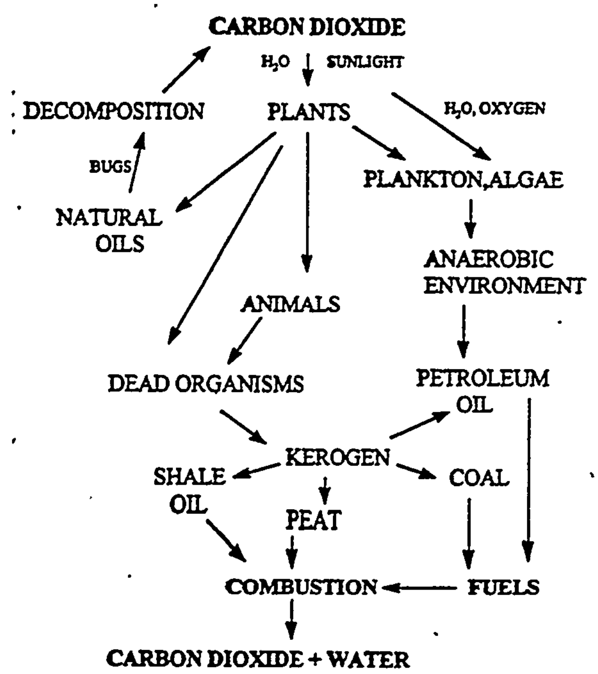


FIG. 4 - ORIGINS OF PETROLEUM

The link between these fossil fuels is carbon. The origin of petroleum is graphically shown on Figure 4. Sea plants and animals were processed by nature in an anaerobic environment for billions of years. The same car-bon cycle resulted in the formation of all carbon containing energy sources.

The first part of this process is called diagenesis and leads to the formation of Kerogen. The diagenesis process is documented in detail in reference [5].

Kerogen is the precursor to a number of fuel products through a process called categenesis. The chemical reactions are driven by temperature and pressure conditions inside the earth In the final step in the cycle. these fuels are combusted and return CO_2 and water to the earth's atmosphere. The type of product formed from Kerogen by the categenesis process depends on whether the hydrogen content is increased or decreased under anaerobic conditions. The process has been going on since time began and is a continuous process.

Depending on the time period, the crude composition differs: California Crudes are relatively new crudes formed during the Cenozoic Era some 60 million years ago. Arkansas, Oklahoma, and Texas crudes were formed some 150 million years ago in the Mesozoic Era, and the oldest crudes, the Pennsylvania and Appalachian, were formed 420 million years ago during the Paleozoic Era. The beginning of the Geological Age was 650 million years ago, the Poterozoic Era Formation of crudes was definitely a slow chemical process. The crudes as a result have different compositions.

This is part of the overall fuel problem since all crudes do not yield the same distribution of straight run products. The Pennsylvania crudes are paraffinic, low in sulfur, produce good quality lubricant distillates but low quality gasoline (RON 49-59). The California crudes tend to be aromatic, high in sulfur, produce little lube stock, but yield a good quality of gasoline (RON 66-73). The refineries take the crudes and optimize the process to produce the desired fuel products, Figure 5.

DIESEL FUEL

During a crisis, the economics dictate the product produced. The approximate fuel distillation ranges are shown on Figure 6. The distillation ranges of gasoline, jet fuel, kerosene, and diesel fuel fractions overlap significantly. During the past oil crisis, the gasoline and jet fuel yields were optimized, resulting in less and lower quality diesel fuels. The European problem was not as severe. They have a higher percentage of vehicle dieselization and their diesel final distillate covers a wider boiling range. This tends to yield better quality (higher octane number) diesel fuel.

More recently, environmental concerns have resulted in low sulfur diesel fuel. The low sulfur fuel results in improved engine emission levels that affect air quality. Initial use of the fuel was not without problems. Engine wear and filter problems, especially at low ambient temperatures occurred. These have been resolved but the low sulfur diesel fuel is a good

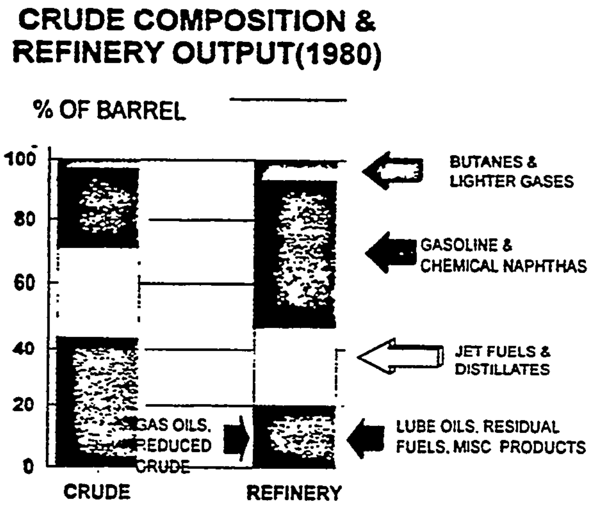


FIG. 5 - CRUDE OPTIMIZATION.

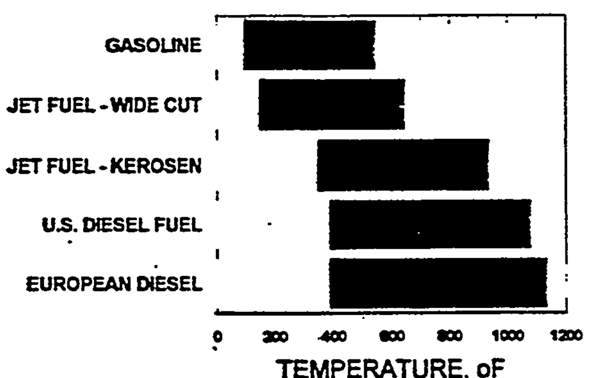


FIG. 6 - REFINERY STRAIGHT RUN DISTILLATION FRACTIONS.

example of the need for adequate research prior to dictating fuel changes.

Biodiesel - a diesel fuel area aimed at reducing the dependence on imported crude and reducing emissions is biodiesel fuel. Use of vegetable oils as diesel fuels is not new. The original use in diesels involved precombustion chamber engines [6]. These engines could tolerate almost any fuel. In the 1970's, these engines were replaced by more efficient direct injection engines. Vega-table oil fuel studies in the 1970's resulted in injector and piston deposits. Methylesters of the fuels performed somewhat better but cost was a factor.

Biodiesel is used in Europe but has not been widely accepted in the U.S. By definition [7], biodiesel fuel is the monoalkyl esters of long chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils and ani-mal fats, for use in diesel engines. It is registered with the EPA as a fuel and fuel ad-ditive in the U.S. The usual mixture of bio-diesel fuel contains 20% methylated vege-table oil and 80 % diesel fuel. Research is needed to optimize the use of the fuel which can impact petroleum diesel fuel use. Diesel trucks used about 15 % of the total trans-portation energy consumption in 1992.

GASOLINE

Gasoline processing has seen a number of changes over the past 40 years. The elemi-nation of lead resulted in the need for ad-ditives to maintain the octane rating required to run automobile engines efficiently. This is done by adding oxygenates to the base fuel. The current oxygenates include alcohols and ethers, Figure 7. The net heat content for the fuels is also shown. The difference between the gross (higher) and net (lower) values is the amount of heat required to vaporize the water of combustion and would be about 5-8%.

Alcohols:	Net BTU/gal (10^3)
MeOH	56.8
EtOH	76.0
IPA	87.4
TBA	94.1
Mixed C1- C5 Alcohols	-----
Ethers :	
MTBE	93.5
TAME	100.6
ETBE	>90
Mixed Ethers	----
Gasoline(C4-C12)	100

FIG.7 - CURRENT OXYGENATES

Some fuel additives such as methanol and ethanol are also used as alternative fuels. Others such as methyl tertiary butyl ether are used strictly as additives. Ethanol is used at levels up to 10% in gasoline (gasohol). Methanol is used at volume levels up to 5% plus 2.5% cosolvents (ethanol, butanol) and corrosion inhibitor. Up to 15% MTBE is used (3.5% oxygen) as a gasoline additive.

Currently, the most commonly used gasoline additives are methanol and MTBE. MTBE is one of the more cost effective additives, made from refinery byproducts. However, some recent health effect concerns have been raised in California where MTBE levels arc accumulating in some lakes and water reservoirs.

ALTERNATE FUELS

Pros and cons of some fuels are shown on Figure 8. Other potential fuels such as tar sands, shale oil products, electricity, hydrogen, and fuel cells are not included at this time. Although considerable progress has been made on these fuels, additional technology development and incentives are re-quired to make these prime candidates. Of the fuels shown, natural gas has the best potential to displace gasoline from petroleum imports in the next 25 years, especially if you consider some of the recent fuel process advancements.

The processing and manufacturing of alternative fuels varies significantly. One of the more exciting developments is the con-version of methane to gasoline. There are two processes well developed to convert methane to gasoline. The SASOL, (Fischer -Tropsch) process and the Zeolite-Socony-Mobil (ZSM-5) process. The first has been used for years to produce gasoline from coal. The second is well developed and is under-going large scale commercialization evalua-tions in New Zealand.

A brief comparison of some of the processing required to produce fuels will further demonstrate some of the advantages and disadvantages of the alternative fuels and the variations used to reformulate gasoline.

Methanol can be made from coal, wood, or other carbonaceous materials. However, it is usually made from cheap, imported, abun-dant natural gas using a highly selective catalyst:

$$CH_4 + 0.5O_2 \rightarrow CO + H_2$$
$$CO + 2\,H_2 \rightarrow CH_3OH$$

Higher alcohols such as ethanol and butanol can also be produced if a less selective catalyst is used:

$$2\,CO + 4\,H_2 \rightarrow C_2H_5OH + H_2O$$
$$4\,CO + 8H_2 \rightarrow C_4H_9OH + 3H_2O$$

Tertiary butanol (IDA), a cosolvent for rnethanoL, is produced by an oxidation process using isobutane and propene.

Ethanol is usually produced by hydration of ethylene, a cheap refinery byproduct:

$$CH_2 = CH_2 + H_2O \rightarrow C_3H_2OH$$

This requires mixing the ethylene with steam at 60-70 atmospheres at ~300°C over a phosphoric acid catalyst supported on a substrate. It can also be made by fermentation of biomass, a process that is being exten-sively researched by USDOE [7].

MTBE, TAME, and ETBE are all widely used ethers in gasoline blending. They are produced from methanol and other refinery products such as isobutylene or isopentene. The downside on all of these from a conservation viewpoint is that they are all made from petroleum. The upside is that they all can be used to upgrade the quality of non-leaded gasoline.

RECENT CONVERSION PROCESSES AND DEVELOPMENTS

To round out the overview on alternative fuel processes, some of the newer more promising developments [7] include:

Shell Middle Distillate Synthesis

A Fischer-Tropsch catalysis process to convert

FIGURE 8

Developed Alternative Fuels

FUEL	ADVANTAGES	DISADVANTAGES
METHANOL	-Vehicles Developed.	-Range 1/2 less gasoline,
	-Flexfuel Vehicles Available	- High costs.
	-Organic emissions less reactive than gasoline.	-Formaldehyde emissions, Cold start problems.
	-Less toxic pollutants	-More toxic than gasoline.
	-Less flammable	-Non-visible flame, explosive in closed tanks.
	- Made from Coal, Wood, Natl Gas, Corn	-Greenhouse problems if made from coal, Corn supply limitations.
	-Abundant Natl Gas	-Probably imported
ETHANOL	-Flexfuel vehicles available	- Range 1/3 less gasoline, high cost
	-Emissions, lower reactivity	- Cold start problems
	-Improved engine efficiency	-Flame - safety
	-Domestic supply source	-Limited supply form corn
	- Enzyme prodn from wood	-Technology cost, development needed
NATURAL GAS		
	-No.Amer. moderate supply	-Imported
	-Excellent emissions	-Possible higher NOx
	-Gas abundant world-wide	-Distribution system
	-Modest greenhouse advantage	-Limited range (LNG = MeOH)
	-Can be made from coal	-Greenhouse problem - coal
	-1mmbd gasoline displaced	-Vehicles, fueling needs research
REFORMULATED GASOLINE		
	-No infrastructure change	-Emissions benefits uncertain
	-Engine modif. not required	-Costs uncertain but significant
	-Applicable to entire fleet	-No greenhouse advantage
	-Economics	-No energy security

[Source: USDOE Office of Technology Assessment, 1990]

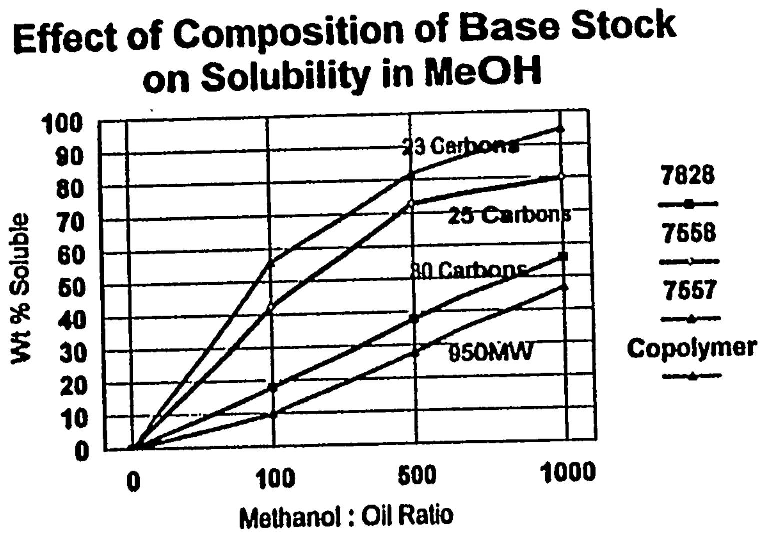


FIG. 9 - BASE STOCK EFFECT.

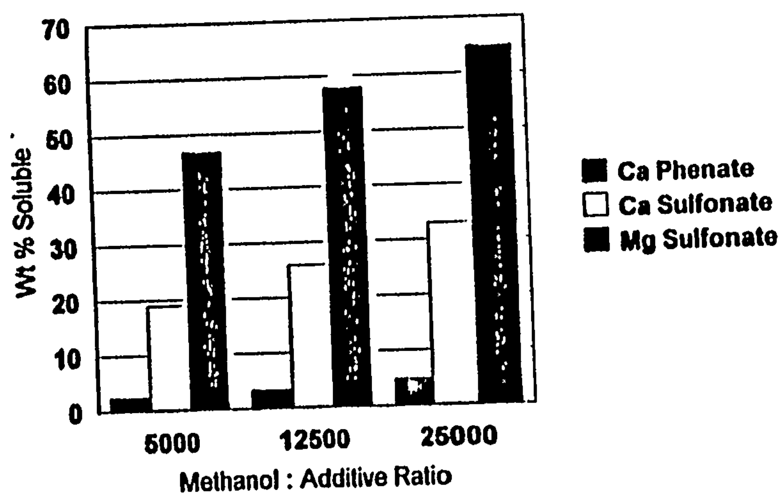
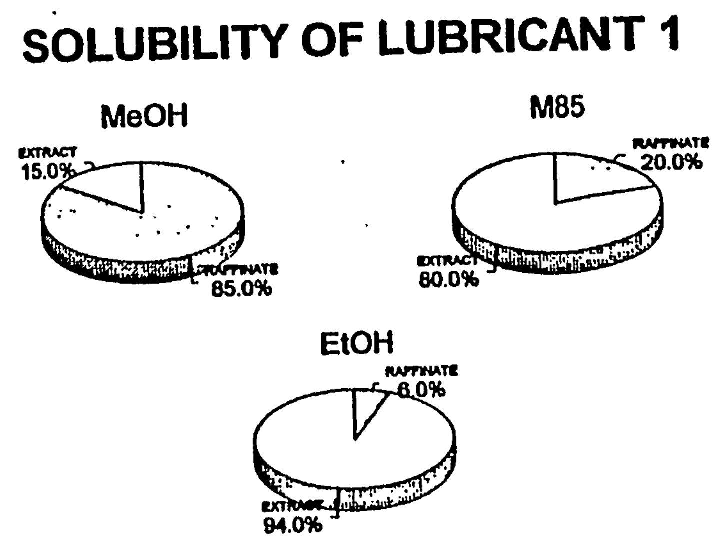


FIG. 10 - SOLUBILITIES OF DETERGENTS.



ADDITIVES EXTRACTED:

	ORIG	MeOH	M85	EtOH
Mg	1150	1100*	550*	<50*
Zn	1100	1000*	700*	0*

* ppm in Extract Phase

FIG. 11 - EFFECT OF FUEL TYPE.

Natural Gas into Transportation Fuels.

The process combines a well proven conversion process with new heterogeneous catalyst technology. The process converts Natur-al Gas into Synthesis Gas and then com-bines the hydrogen and CO in a molar ratio of 2:1. SMDS is technically proven and commercially viable. A pilot plant is opera-ting in Bintulu, Malaysia.

<u>Dimethyl Ether (DME) from Coal</u>

NKK Corporation, Tokyo, Japan, reportedly has developed a DME process. Production is at the stage where NKK claims DME can become a practical energy source for home use, electrical power generation, and transportation.

<u>Synthesis of Fuel alcohols and MTBE from Syngas</u>

Union Carbide has reported development of a catalyst system for the synthesis of near equal mixtures of methanol and isobutanol from syngas. These products are then used to synthesize MTBE, a preferred gasoline octane booster.

<u>Liquid Phase Methanol (LPMeOH™)</u>.

Air Products and Chemicals, Inc., have a commercial scale (150,000 g/d) demonstration plant for Integrated Gasification Combined Cycle (ICGG) power generation applications. Technology yields methanol at $0.50/gallon. The process can use syngas from coal gasification process and is a once-through catalyst system

<u>Natural Gas to Synthetic Petroleum Liquids via the Syntroleum Process</u>

The Syntroleum Process is a proprietary method for converting natural gas into liquid hydrocarbons (GTL), reportedly competitive with current oil prices. It is a modification of the Fischer-Tropsch process and uses a autoreforming step using air to partially oxidize the natural gas.

LUBRICANTS

One last area that should be considered in researching alternate fuels is that the entire system needs to be considered. Lessons learned from the conversion of the use of methanol in both gasoline and diesel engines should be remembered. Not all lubricants and fuels are compatible. Studies at Penn State University [8,9] have shown extraction of additives occurs readily with methanol ethanol and M85. The solubility of both the base stock, Figure 9, and the additive pack-age need to be evaluated, Figure 10. In addition, the extraction of the lubricant is close-ly tied to the type of fuel, Figure 11. The lubricant must be designed to function in a system where fuel contamination can result in appreciable depletion of the functionality of the additive package.

SUMMARY AND CONCLUSIONS

FUTURE TRENDS

The major factors that can significantly affect the rate of change to alternative fuels are shown on Figure 12.

RATE OF CHANGE CAN BE AFFECTED BY:

1. **CRUDE OIL PRICES**
2. **NATIONAL SECURITY**
3. **ENVIRONMENTAL CONCERNS**
4. **VEHICLE TECHNOLOGY**
5. **ECONOMICS/PRODUCT SELECTION**

FIG. 12 - MAJOR FACTORS

They are listed in order of influence in the current climate. The price of crude is stable. As long at it stays this way there is little incentive to accelerate current production. Price supports or tax incentives for new fuels and infrastructure are not the long term answer.

The life blood of U.S. industry is petroleum. Any. threat to national security will affect prices and result in increased reactivity. Continued efforts to establish alternative fuel strategies will soften any future crisis affecting petroleum irnports.

Environmental concerns are a constant is-sue. Controversy over the impact of diesels, alternate fuels, and reformulated gasoline continue. Health effects of diesels are still unresolved and are not without controversy. Foreign dieselization is significantly ahead of the U.S. and a positive approach to energy conservation. Coal processed fuels are very high in aromatic compounds. This improves the octane rating of the products which is significantly undesirable if looked at from a health effects issue. The impact of the alternate fuels on air quality are positive but not without problems. The aldehydes produced by alcohol fuels on cold startup or in poorly maintained catalysts are still issues to be resolved.

New engine technology including electric, hydrogen and fuel cell vehicles has made some progress but is not readily available technology. The improvements in the combustion efficiency of current SI and CI engines have made significant impact on fuel economy and engine emissions. The re-search on advanced diesels requires additional support.

Most chemical processing to produce alternative fuels is not economically competitive with petroleum at the current time. The research, especially to convert natural gas and methane to gasoline and diesel pro-ducts, needs to continue to search for better processes. As petroleum availability decreases, prices will go up and economic is-sues should dissolve.

Lubricant research on the tribological aspects of the new fuels needs additional effort.

SCENARIOS

The following scenarios could have a significant impact on petroleum conservation and use:

1. If oil prices increase rapidly or national security factors occur, development of alterative fuels will accelerate along with the cost of petroleum.

2. If oil prices remain stable, then environmental concerns and considerations, and advanced technology will be driving factors in use of alternative fuels.

3. Decreasing crude quality will result in poorer fuel quality. This will result in more interest in additives, such as surfactants, and cetane improvers.

4. Biomass and coal become more important as the reserves decrease and processing economics become more favorable. This will take some 25 years or another oil crisis.

5. Renewable resources will make inroads as lubricant base stocks and diesel fuels as economics improved. The technology is demonstrated. However, the use volume of lubricant products is so large, current production of vegetable oils could not meet the requirements. The use of these lubricants could impact the dependence on imported oil. It could also help third world countries whose economies now depend on petroleum. Further inroads could be made if technology is developed to significantly extend drain periods for alternative fuels and lubricants. Recycling technology is another need.

The main competition to renewable fuels and lubricants resources will be the need for food as the earth's population continues to expand uncontrollably. Research to achieve better crop yields and better quality vegetable oils is needed.

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