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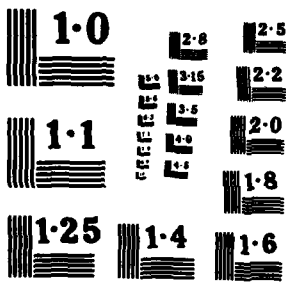
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DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION
MATERIALS RESEARCH LABORATORIES
MELBOURNE, VICTORIA

VEGETABLE FUEL POTENTIAL

by

Richard K. Solly

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ORGANIC CHEMISTRY DIVISION
TECHNICAL REPORT

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ABSTRACT

The possible contribution to Defence fuels from vegetable sources is considered. Only two categories, ethyl alcohol from fermentation of carbohydrate material and vegetable oils directly from oil crops, can currently be produced with present technology in sufficient amounts to contribute to energy requirements. Liquid hydrocarbons from tree and shrub crops or microorganisms have not been produced in sufficient quantity to carry out even short term engine trials. Ethyl alcohol is an effective gasoline extender for spark ignition engines, but these are a minor part of Defence power units. Vegetable oils may be directly substituted for middle distillate fuels, but a number of technical difficulties are outlined. Chemical reaction of the vegetable oils with ethyl alcohol produces a liquid fuel which has similar physical properties to petroleum distillate. Experimental and theoretical evidence suggests these vegetable oil esters have better combustion properties in compression ignition power units than petroleum distillate. Significant amounts could be produced in a strategic situation within a short lead time.

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Tristhan; ester; fuel alcohol.*

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VEGETABLE FUEL POTENTIAL*

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VEGETABLE FUEL POTENTIAL

1. INTRODUCTION

Vegetable fuel in the form of wood was the earliest fuel used by man. It still makes a significant contribution to energy requirements, particularly in developing countries. As a relatively low energy density solid fuel, it is not likely to be cost effective with coal as an industrial and strategic fuel. Known coal reserves are sufficient for several hundred years at presently estimated rates of consumption. On an international basis and particularly with respect to Australia, coal can readily meet all solid fuel requirements.

It has been variations in the availability of liquid fuels which have triggered considerations of an energy crisis. Small shortfalls in international requirements have led to large price increases in petroleum fuels. With the price increase, the economic viability of many alternatives to liquid petroleum fuels has greatly increased. Conversion of coal, natural gas and oil shale to liquid hydrocarbon fuels have been the subject of greatly intensified investigations, but are outside the scope of this presentation. Consideration will be given to crops which may be grown for conversion to liquid fuels. With modern technology, the number of possible crops is very large. Any carbon source (either organic or inorganic) may be converted to liquid fuels after gasification to carbon monoxide and synthesis with hydrogen. This potential is far too broad to be considered in this discussion. Three categories of crops will be considered. Firstly, those which can yield liquid hydrocarbons directly or with solvent extraction. Secondly, those which yield a starch or sugar which may be fermented to a fuel alcohol. The third category is crops producing a non hydrocarbon liquid which may be used directly as a fuel or after simple processing.

2. LIQUID HYDROCARBON YIELDING CROPS

Typical of this group of crops is the rubber tree (*Hevea brasiliensis*). A polyisoprene is produced in the form of a latex rubber. Cracking of the polyisoprene material is required to produce a range of hydrocarbon fuels. The rubber tree requires high rainfall, good soil and tropical conditions for best growth. Most attention in these types of crops has been focussed upon those which can grow in semi-arid climates. Land which is unsuitable for other agricultural uses might then be used for the growth of crops to produce liquid fuels. Many hundreds of species has been proposed in this category. In addition to a hydrocarbon fraction, almost all plants also contain a carbohydrate fraction. This may also be utilized to produce energy.

Yields of liquid fuels from this range of crops is open to much debate. In Australia, much attention has been focused upon *Euphorbia lathyris*, which can grow in semi arid tropical and

sub tropical areas. From this species on an estimated yield of 10.2 tonnes per hectare which may be obtained without irrigation, the potential energy was 65 GJ/ha/year and 52 GJ/ha/year from the liquid hydrocarbon components and the carbohydrate components respectively. This is equivalent to the energy content of 1.76 and 1.41 kilolitres of middle distillate fuel respectively. In order to obtain these fuel materials, solvent extraction of the biomass is required. Currently this process is slow and not economically viable. Due to the very high cost, the total production of liquid fuels from these crops is currently very small. This amount is likely only to be sufficient to operate a single standard production internal combustion engine for less than a single day. The minute amount of liquid fuels that are currently available from these sources does not give rise to confidence that they can make a significant contribution to strategic fuels requirements within present economic and technical conditions.

Photoplankton species, including *Botryococcus braunii*, may also produce hydrocarbon oils. That extracted from *Botryococcus* has hydrocarbons containing predominantly 34 to 40 carbon atoms. These may be hydrocracked to yield lower molecular weight hydrocarbons with a very low proportion of aromatic and olefinic species. Collection and extraction of the biomass from *Botryococcus* presents many technical and economic problems. Collection and processing of photoplankton on a large scale provides further technical hurdles. As with the higher plants as a direct source of liquid hydrocarbons, large changes in technical economic conditions are required for photoplankton to be considered as a significant source of liquid fuels.

3. CROPS FOR FUEL ALCOHOL PRODUCTION

This category of crop has received the most attention in relation to the production of liquid fuel. Ethyl alcohol (ethanol) is produced by microbial fermentation of sugars. Sugar polymers such as starch and cellulose can be fermented to alcohol after chemical or enzymatic hydrolysis to the simple sugars. As almost all crops contain cellulose, they are a potential source of ethanol. However, the hydrolysis of cellulose is a difficult process and cellulose cannot currently be considered a feasible material for the production of ethanol. Presently Australia produces approximately 100 megalitres of ethanol per year from molasses, a byproduct of the sugar refining industry.

Ethanol has excellent combustion characteristics when used as a fuel in a spark ignition internal combustion engine with a research octane number of approximately 108. Conversely, it is a poor fuel in compression ignition engines with a very low cetane number. However, the energy content of ethanol is only 59

per cent that of gasoline and a high heat of vaporisation gives rise to cold starting problems and fuel vaporization problems. These preclude the use of 100 per cent ethanol in unmodified gasoline engines. It is most readily utilized in gasoline blends of up to 20 per cent ethanol. Cold starting and elastomer problems are minimal as is phase separation of the liquids.

Ethanol gasoline blends are available commercially as a fuel in the United States and Brazil and these blends have been the subject of extensive studies. The technical feasibility of ethanol as a fuel is well established. Similarly the technology for production of ethanol from a carbohydrate feedstock is well known. Most current investigations are directly towards the technology and economics of carbohydrate crops. Molasses is the major feedstock for ethanol production, although starch from grain crops and sugar in the case of Brazil are significant. The high yielding tropical root crop, cassava, is widely advocated as a starch feedstock for ethanol production. Only in Brazil does it make a small contribution to the total alcohol production. Small scale trial production of cassava is currently under investigation in Australia. In the immediate term, it is sugar (cane or beet) and grain crops which have the most potential to make a significant contribution to alcohol production. The Australian CSIRO has estimated that by doubling Australia's sugar cane and grain production, ethanol could contribute 25 per cent of the gasoline demand in 1980. Clearly ethanol has the potential to make a significant contribution to gasoline requirements. However, the most ready use is in admixture with gasoline. The Defence forces use of gasoline is relatively small and limited to light vehicles and light aircraft. Both power units may be replaced with distillate powered equivalents. Gasoline or gasoline substitutes have a low significance as defence fuels. Ethanol may be used in admixture with distillate fuel in compression ignition engines. However the cetane number of the mixture is reduced and anhydrous ethanol does not form a stable one phase mixture in higher proportions than approximately 10 per cent with most distillate fuels. It is more feasible to reserve ethanol as a fuel extender for gasoline engines.

4. VEGETABLE OIL CROPS

Vegetable oil is the other potential liquid fuel crop with ethanol which is presently produced worldwide in million tonne lots. Vegetable oils are the triglycerides of the long chain fatty acids. The triglyceride molecule has three fatty acid carbon chains attached to the ester groups of the glyceride. Each fatty acid chain consists predominantly of from 12 to 22 linear carbon atoms. Considering oxygen atoms as being equivalent to carbon atoms, a triglyceride molecule contains from 45 to 75 equivalent carbon atoms. Petroleum automotive distillate fuel contains molecules with approximately 10 to 30

carbon atoms. Hexadecane, the standard cetane index fuel for the compression ignition engine, contains 16 linear carbon atoms. Long chain paraffin hydrocarbons have good combustion characteristics in the diesel engine. The combustion characteristics and cetane numbers of vegetable oil are approximately equivalent to petroleum diesel fuel. Due to the presence of the oxygen atoms in the molecule, the combustion energy per litre is approximately 5 per cent less than petroleum distillate. The major differences arise from the much larger molecular size of vegetable oils. The viscosity, vapour pressure and flash point of vegetable oils are much greater than distillate fuel. Data for a range of fuel characteristics are shown in Table 1. These values represent a synopsis of available data. As the composition of vegetable oils may vary significantly, values were chosen to represent a self consistent mean.

TABLE 1
PROPERTIES OF VEGETABLE OIL FUELS

	SFO	RSO	MeSFO	ETOH	DIESO
<u>Viscosity (40°C)</u> mm ² /S	32	34	2.4	1.3	2
<u>Density (40°C)</u> kg/l	0.91	0.91	0.87	0.77	0.85
<u>Cloud Point</u> °C	-6	-5	+1	-114	-1
<u>Flash Point</u> °C	320	340	185	18	60
<u>Calorific Value</u> MJ/l	36.6	36.8	35.2	21.0	38.8
Cetane Number	34	35	49	-	45

SFO Sunflower oil
RSO Rapeseed oil
MeSFO Methyl ester sunflower oil

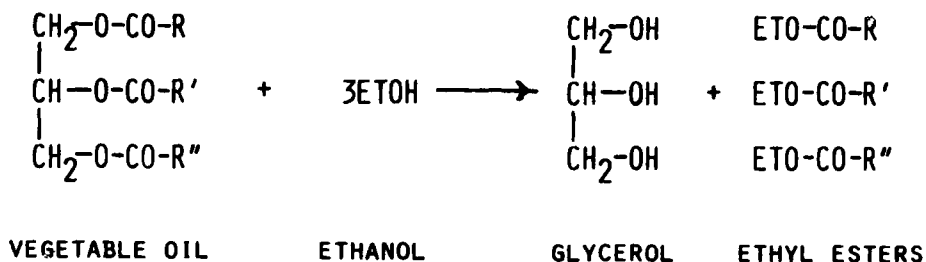
A number of trials with vegetable oil as a fuel substitute for petroleum distillate fuel were carried out during the time of the Second World War. In all cases the engine operated successfully on the vegetable oil fuel in the initial stages. Reports then indicated some problems with filter

blockage due to impurities in the oil and deposits forming on the injectors. The petroleum shortfalls of the 1970s provided a further impetus for investigation of the use of vegetable oils as fuels. Many thousands of vehicle hours have now accumulated with vegetable oils. Whereas these trials cannot be regarded as comprehensive or conclusive, definite trends are apparent.

As found previously, all vegetable oils will operate compression ignition engines for at least a short period. With extended operation, two categories of problems become apparent. The first is blockage of engine filters due to the presence of impurities and the high viscosity of the vegetable oil fuel. The second category is associated with the formulation of engine deposits. Injector deposits has been widely reported for engines operating on vegetable oil fuels. These injector deposits may result in poor atomization of the fuel and a subsequent increase in the rate of formation of the deposits. Poor atomization leads to an increase in specific fuel consumption and the possibility of non combusted fuel entering the crankcase oil. Vegetable oils in general are very reactive towards the antioxidants in crankcase oils. Upon depletion of the antioxidants, the crankcase oil rapidly deteriorates with a large increase in viscosity and loss of lubricating properties. Other deposits have been reported on the piston crowns and associated with sticking piston rings and subsequent breaking of the rings.

Considering these problems, can vegetable oils be considered a feasible fuel? As an alternative to and exchangeable with petroleum distillate the answer is clearly in the negative. Handled similarly to petroleum fuels, vegetable oils would only operate diesel engines for a relatively short period before the occurrence of one or more of the known problems. If the shortcomings of vegetable oil fuels are considered in the operating procedure and engine maintenance is programmed towards the problem areas, operation could be almost indefinite. More maintenance directed particularly towards crankcase oil changes, fuel filter changes and injector cleaning would be required than is the normal practise with current petroleum fuels.

It is possible to chemically modify vegetable oils by transesterification with alcohols. Methanol and ethanol are the most readily available alcohols and yield the methyl or ethyl esters of the vegetable oil fatty acids respectively. This is a relatively simple chemical process and the molecular size of the ester is approximately one third of the corresponding vegetable oil.



Esters of vegetable oils have a long chain carbon structure similar to that of the fuel standard cetane (hexadecane), which is the reference point at 100 for the engine determination of cetane numbers. The molecular size of the esters is also similar to that of the average molecules making up petroleum distillate and as would be expected the viscosities are similar. Due to the presence of the oxygen atoms in the molecule, the energy content is 5-10 per cent less than petroleum distillate as may be seen from Table 1.

It is only in the recent two or three years that longer term engine trials have been conducted with the methyl or ethyl esters of vegetable oils. The Volkswagen Company of Brazil has operated a 1588 c.c. four cylinder swirl chamber engine for 1400 hours on a test rig with the methyl esters of soybean oil as fuel. During this operation, 1000 hours were at maximum power and 300 hours at maximum torque. The crankcase oil was drained each 75 hours of operation and the viscosity, total acid number and total base number of the used oil determined. Despite the vigorous test conditions all values for the used oils remained acceptable. Values of torque, power, smoke levels and cylinder compression remained within variations expected for this test. The engine was dismantled and clearances between critical engine components measured. Each of the eight clearance determinations were representative of normal results in this test. The Bosch rotary injection pump which was lubricated by the ester fuel only, showed no abnormal wear. Deposits in the combustion chamber and around the nozzles were dry, soft and easily removable and possibly slightly below normal for petroleum fuels.

A Diesel Passat and a Diesel delivery van are also being tested with the methyl esters of soybean oil as fuel. At the time of the report, the Passat had operated 40,500 km on the ester fuel. Driveability, performance, engine noise and cold starting were comparable with operation on petroleum distillate fuel. Concentrations of carbon monoxide and nitrogen oxides were measured in the exhaust gases. Carbon monoxide levels were reduced 40 per cent for the ester fuel with nitrogen oxide levels remaining the same. Analyses of the oil at each 7,500 km change showed no abnormalities.

Esters are good solvents for organic materials. A number of elastomers have been immersed in the methyl esters of soybean oil for up to 50 hours at room temperature. Whereas some elastomers such as viton and polyformaldehyde showed comparable deterioration in the ester compared to the distillate, many elastomers including nitrile rubber, polyamide and polyurethane deteriorated to a greater extent in the liquid ester. The adhesives in some brands of fuel filters are also dissolved by the ester fuel. The solvating properties of the esters may be beneficial in some applications. The esters increase the solubility of icing inhibitor agents in distillate and minimize mixing problems.

The total number of hours of internal combustion engine operation on either vegetable oils or their esters is very small. From the thousands of hours operation on vegetable oil fuels, problems with filter blockages, injector deposits and engine deposits are much more prevalent than with petroleum distillate fuels. If engine maintenance were designed to rectify these problems, vegetable oils could be used as a fuel over long periods of time. Engine operation with the esters of vegetable oils is much more limited than that for the triglyceride oils themselves. From the limited data, the combustion properties of the esters are possibly better than current automotive distillate fuel. This is to be expected as the long carbon chain structure of the esters is similar to that in cetane. Whereas petroleum distillate contains many types of hydrocarbon molecules with inferior combustion characteristics to cetane, esters of vegetable oils contain only long chain compounds.

Within Australia, the potential of vegetable oil fuels is a component of the Crop Fuel Programme of CSIRO. It is estimated that five million hectares of oilseeds would produce approximately 20% of current distillates consumption. This level of cropping could be achieved with conventional cultivation and without reducing current crop production. Using improved tillage technology and new varieties of oilseeds, the production could reach the equivalent of 35-40% of current Australian automotive distillate consumption. The current area cultivated for oilseeds in Australia is approximately 350 thousand hectares from which approximately 5% of an automotive distillate fuel substitute could be obtained. Australian Defence Forces presently consume 1.2% of the national automotive distillate requirements. Thus in theory, present Australian production of vegetable oils could meet both peacetime and contingency energy requirements by the Defence Forces for automotive distillate. While it is more likely that vegetable oil fuels would contribute to strategic requirements of the farming community, the esters of vegetable oils in particular could meet most Defence distillate requirements.

5. CONCLUSIONS

In the short and medium term, only fuel crops providing ethanol from carbohydrates and vegetable oils have the potential to make a significant contribution to Australian strategic fuel requirement. Ethanol is a substitute for gasoline and thus has limited application as a Defence fuel. Vegetable oil may be used directly as a petroleum distillate substitute but technical problems are likely to limit the utilization. Simple modification of vegetable oils by chemical reaction with ethanol produces the esters of the vegetable oils. These esters would appear to have better combustion properties than petroleum distillate and compared to petroleum fuel, only limited problems with materials compatibility, storage stability and possibly lubricating oil interaction. In a petroleum shortfall situation, current production of vegetable oils could be rapidly directed towards a small but significant contribution to automotive distillate fuel requirements. Within a growing season, present cereal cultivation areas could be diverted to production of oilseeds with an order of magnitude increase in the production of a petroleum distillate substitute.

Due to the relatively low energy density per unit area for production of fuel crops, they can never meet the energy demands currently supplied by fossil fuels. In a petroleum supply shortfall situation, fuel crops yielding ethanol or vegetable oils have the potential to make a small but significant contribution to total liquid fuel requirements. The lead time for this contribution is very much less than that required for the production of liquid fuels from oil shale or coal liquification.

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