Thermochemical Applications for Fats and Oils

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ABSTRACT

Fats and oils are well established in food, surfactant and coatings applications. Historically, fats and oils were employed to provide lighting and warmth. Increasing production of fats and oils and increasing uncertainties regarding the reliability of petroleum resources make it desirable to reconsider thermochemical applications of fats and oils. Difficulties associated with the use of fats and oils for vehicular applications are discussed, and use in stationary diesel engines is suggested.

Conventional kerosene space heaters are designed to make use of the vaporization behavior of this fuel. Changes in heater design are required to take into account the pyrolytic degradation of the fuel when fats and oils are used, and a traveling grate burner was designed for this purpose.

Pyrolysis of fatty acids at temperatures exceeding 500 C yields a mixture of gaseous and liquid products. The gaseous products include ethylene, but little propylene. The liquid product is primarily a mixture of substituted styrenes.

Further development is needed for these thermochemical applications of fats and oils. Fuel and olefin markets present valuable cushions to keep the price of fats and oils from fluctuating as during the early 1980's, when soybean oil has varied from $0.15 per pound to $0.40 per pound. The triglycerides can provide a future source of feedstocks for petrochemicals, if petroleum prices and availabilities change dramatically. Most of the development work needed consists of down-to-earth large-scale experiments in semi-commercial or commercial equipment to determine the best methods of fuel storage, feeding and conditions for combustion and steam cracking.

INTRODUCTION

Fats and oils are well established in food, surfactant and coatings applications where their price/performance characteristics allow them to compete well with modern petrochemicals. Before petroleum and natural gas became dominant fuels, fats and oils provided light and heat for a significant percentage of the population of many countries. These thermochemical applications became historical curiosities when the kerosene lamp and the electric light bulb displaced the whale oil lamp and the tallow candle.

Periodic over-production of fats and oils in which more triglycerides are produced than the market is able to absorb is an economically destructive phenomenon. Inventories build up, requirements for credit increase, low farm prices prevail, rural banks suffer, farm equipment sales decline and government assistance programs burden taxpaying consumers. Because of these adverse effects, it would be desirable to have an underlying market for fats and oils that could absorb the surpluses as they form. Fuel markets could absorb periodic fats and oils surpluses, because fuel demand is large compared with the surpluses of fats and oils.

In China (1,2), Europe (3) and the United States (4), there have been sporadic attempts to make short chain olefins from fats and oils, primarily during wartime shortage conditions. Relatively little progress was made along these lines because the acute shortages were relieved before much was accomplished.

The concurrence of a period of low soybean oil prices during the early 1980's, the boom in kerosene space heater sales and projected high prices for petroleum and petrochemicals prompted researchers at Battelle-Columbus to conduct some investigations into the feasibility of using fats and oils as fuels and as feedstocks for production of olefins. This paper provides some information concerning the results of these studies.

EXPERIMENTAL

Traveling Grate Burner

The overall layout of the apparatus used in these proof-of-concept experiments is shown in Figure 1. Its purpose is to allow the moving grate to pick up fuel, carry it to the flame zone and return to pick up more fuel. The arrangement of the rollers is such that if the moving grate or belt travels in the forward direction (left to right on Figure 1), it produces an ascending burning surface, while belt travel in the reverse direction (right to left on Figure 1) produces a descending burning surface. All of the rollers are on shafts fixed to a 6 mm thick aluminum backplate. One of the rollers is driven by a variable-speed gear motor to allow changing the linear speed of the moving belt. The rollers are 38 mm in diameter and have a circumference of 120 mm. A shallow pan holding about 1.5 l of fuel was used to saturate the mesh belt prior to the burning zone.

The mesh belt was 74 mm wide and 1540 mm long. The mesh was formed by a screen of 0.26 mm diameter brass wire with openings 1.8 mm square. The screen had a mass of 606 g/m^2.

Both corn oil and kerosene oil were burned in the moving grate burner. A cooking grade of corn oil was used. The kerosene was 1-K grade, used with fire precautions.

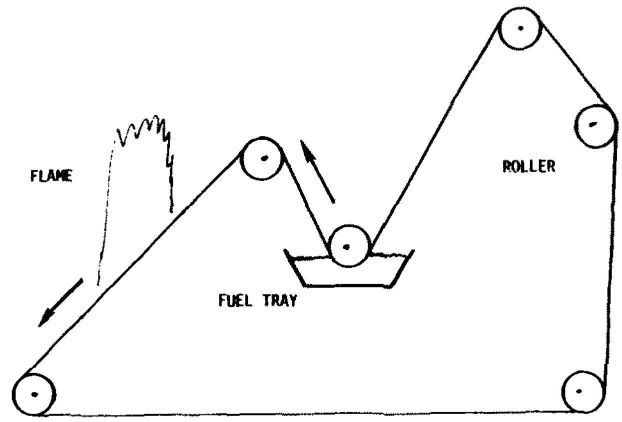

FIG. 1. Overall plan of traveling grate burner.

Laboratory-Scale Steam Cracker

The steam cracking experiments were conducted using the apparatus shown in Figure 2. The hot zone of the quartz pyrolysis tube has an inside diameter of 5 cm and is 61 cm long. The contact time at 600 C is three seconds. The steam/fatty acid ratio is 10:1. The fatty acid feed rate is 0.33 g/min. The water feed rate is 3.3 ml/min.

The fatty acids were obtained from Sigma Chemical Company, St. Louis, Missouri. The fatty acids were approximately 99% pure by manufacturer's analysis.

The gas chromatograph employed for analysis of the pyrolysis products is a Carle Model 111 H, equipped with an H_2 separator. The analyses were conducted isothermally at 65 C using a thermal conductivity detector. A second gas chromatograph using a Tenox column and an FID detector was used to measure the trace hydrocarbons.

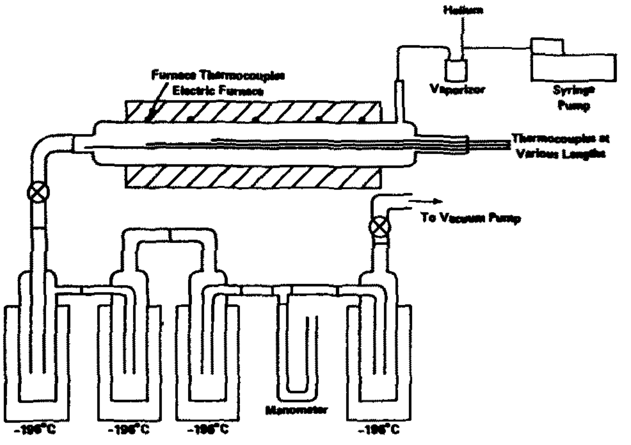

FIG. 2. Laboratory-scale steam cracker.

RESULTS AND DISCUSSION

Fats and Oils as Fuel

Considerable research and development has been conducted under the sponsorship of Federal and state governments with one type of potential multiple fuel burner, the diesel engines for farm equipment and trucks (5,6). Our evaluation of this end use application indicates that this is a demanding use (7). Diesel engines for outdoor vehicular applications frequently operate under adverse weather conditions (8). The operators of the diesel engines may or may not be knowledgeable as to the best procedures to use for starting and maintaining the engines. Even when they are, the rigors of farming or truck driving may not allow the best practices to be used. The numerous studies conducted in the United States by agricultural engineering organizations, research institutes and engine manufacturers demonstrate that this is an attractive application in principle and from a market viewpoint, but a very difficult application from a practical viewpoint.

While we and others were evaluating vehicular diesel engine applications, we also examined steam and electric power generation using fats/oils. The generation of electric power and/or steam and electricity appears to be a much more attractive application when all factors are taken into consideration (9). A stationary diesel electric facility could make use of fats or oils more readily than could diesel vehicles. Steam and electricity can be generated from fats and oils by using a conventional liquid fueled boiler or a gas turbine that normally consumes No. 2 diesel fuel oil. The combustor may be operated in an electric utility or an industrial steam and/or electricity mode. These devices are already in place; it would not be necessary to design new equipment or for the utility or industrial company to make major capital investments (10). Some retrofitting would be needed.

Most industrial companies and utilities have maintenance personnel dedicated to their combustion equipment. The equipment frequently operates for a relatively long production run compared with the intermittent operation of farm equipment and other over-the-road or off-the-road vehicles.

Although the development of fats and oils for utility and industrial combustion applications is much easier than it is for diesel-powered vehicles, there is research to be done to adjust the fuel feeding and combustion system to accommodate the higher viscosity and freezing points of triglycerides and the cracking reaction mechanism by which they burn. In addition, fuel storage and fuel use equipment have to be compatible with the constituents of fats and oils (e.g., free fatty acids).

In addition to this optimization research, it would be necessary to build up a marketing and distribution system for this somewhat paradoxical application. It is termed "paradoxical" because use of fats and oils in these applications will not occur every year. For example, in May 1984, soybean oil was $0.40 per pound; who wants to burn $0.40 per-pound soybean oil when No. 2 diesel fuel is available for $0.15 per pound? When the price of diesel fuel rises and/or the price of fats/oils declines to a crossover point, a few sizable purchases of fats or oils by the fuels industry may reverse the crossover. Thus, the marketing system must be capable of operating intermittently.

A Multi-Fuel Combustor

In addition to the large-scale combustors that make use of atomizers to introduce liquid fuels, it would be desirable to have a combustor design that would function at a much smaller scale. A good example would be a replacement for the kerosene space heater that was cited by Consumer Reports (11) and many fire marshals for its fire safety hazards. Kerosene space heaters make use of wicks (12) that are not suitable for fats/oils because not enough fuel can be brought to the point of combustion per square foot of wick per minute. Also, the heat feedback from the flame to the incoming fuel was insufficient to heat the incoming oil to its fire point. We did demonstrate that solutions of fats and oils in kerosene would burn effectively. However, the problems of fire safety, handling kerosene and toxicity of the sulfur compounds in inexpensive kerosene would remain as problems if this approach were used. Therefore, an alternative burner design was sought.

For a fats/oils fuel system to be effective, it is important that the combustion system provide easy interchange between fats/oils and petroleum or natural gas-based fuels. If the fats/oils combustor could use only the renewable product and not the competitive fossil fuel, price increases in fats/oils could render the combustor uneconomical to use. Therefore, the Battelle research has concentrated on multiple fuel combustors that are capable of using various fuels depending on their relative prices.

A traveling grate concept was selected because it was capable of burning a substantial quantity of triglyceride per min per sq ft. Depending on the specific application, the traveling grate could be operated electrically or more likely by using a windup device. The energy required to turn the traveling grate for hours can be stored with a windup device. There is an added safety feature in that the device is easy to set to turn itself off after specified periods of time.

A prototype traveling grate burner was constructed and operated with soybean oil and with No. 2 diesel fuel. The flame not only acts as a space heater but also serves to crack the liquid fuel so that actually a mixture of gases, not the liquid, is the fuel. This burner was able to sustain a reasonably stable flame in the downward moving section of the belt (Fig. 1). With the resources available at the time, no attempt was made to optimize belt speed, slope, etc., and the air supply was uncontrolled.

It is clear that the major optimization problem will be elimination of soot as a combustion product. A more carefully regulated air supply will be needed to eliminate the soot. If a blower proves to be necessary, the traveling grate burner may be useful for commercial or industrial applications but would lose its attractiveness as a household space heater. A patent search revealed a somewhat similar device (13), but it is not clear to what extent it was commercialized.

Olefins from Biomass

The markets for simple olefins such as ethylene and propylene are huge. For example, more than 25 billion pounds per year of ethylene are sold at approximately $0.26 per pound (14). The world relies almost exclusively on natural gas (in the U.S.) and heavy petroleum fractions (in Europe) for olefin feedstocks. These fossil feedstocks are subject to changes in price and/or availability that are associated with recurrent energy crises. New olefin plants are huge and costly. They produce numerous coproducts, each of which must be sold at reasonable prices to attain profitability.

In principle, these simple olefins appear to be a highly attractive set of products to make from fats and oils. The olefin transformation products (e.g., polyethylene, polyvinyl chloride, ethylene glycol and acrylonytrile) are well established in their respective end-use markets.

In Brazil, ethylene and vinyl chloride are being made from ethanol that is derived from sugar cane juice (15). It requires about 100 lbs. of sugar to make 30 lbs. of ethylene. Brazil is subsidizing this technology because it consumes sugar that would be difficult to sell in the world market and it is building experience in the technology for the day when ethylene prices will be high. In addition, domestic production of ethylene and vinyl chloride by this route saves foreign exchange. However, the technology holds little attraction in the U.S.

We examined thermochemical cracking of fats and oils. There is a rich literature on this subject, but the yields of ethylene, propylene and other useful products are quite poor. The literature that we examined did not reveal the use of steam cracking of fats and oils. Because that is the way that reasonable yields of ethylene and propylene are obtained now from hydrocarbons, we decided to apply this modern approach.

Using the device shown in Figure 2, we steam cracked stearic acid, oleic acid and linoleic acid. Each fatty acid has a distinctive product distribution. Typical results obtained with oleic and linoleic acid are given in Table I. The overall yields of gaseous products are sensitive to the temperature at which the cracking reaction occurs. The major products were methane and ethylene. There also were smaller quantities of C_3+ olefins, carbon monoxide and carbon dioxide. The gas yields approached 100% in some cases. The liquids were identified as a complex mixture of aromatic hydrocarbons, primarily substituted styrenes.

There appear to be considerable opportunities to improve this steam cracking technology. From a research and development viewpoint, gentler, catalyzed steam cracking would be desirable. This could lead to olefins longer than ethylene and to retention of the carboxyl group and formation of short chain fatty acids. From a commercial viewpoint, it may be more valuable to subject substantial quantities of fatty acids to conventional steam cracking under the conditions now used by the steam cracking industry. These experiments could enable industry planners to determine where in the price hierarchy specific fats and oils stand compared with petroleum hydrocarbon feedstocks.

TABLE I

Gaseous Products from Steam Cracking of Fatty Acids

		Gas composition, wt% of acid introduced						
Acid	Temp. C	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3+	Total
Oleic	500	<1	1	<1	1	<1	1	4
	600	10	12	27	48	<1	2	100
	700	6	9	13	30	1	16	75
	800	12	12	22	48	<1	4	98
Linoleic	600	7	11	18	30	<1	–	66
	700	11	7	12	24	<1	2	55

Further development is needed for these thermochemical applications of fats and oils. Fuel and olefin markets present valuable cushions to keep the price of fats and oils from crashing during the volatile 1980's that already have experienced soybean oil at $0.15 per pound and $0.40 per pound. The triglycerides can provide a future source of feedstocks for petrochemicals, if petroleum prices and availabilities change dramatically. Most of the development work needed consists of down-to-earth large-scale experiments in semi-commercial or commercial equipment to determine the best methods of fuel storage, feeding and conditions for combustion and steam cracking.

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