Transesterification of Vegetable Oil
for Use as a Diesel Fuel
-- A Progress Report --

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SUMMARY:

This paper discusses procedures for producing
the methyl ester of winter rape oil for use as
a diesel fuel substitute and gives a brief
report of research directed toward producing
the ethyl ester of winter rape.

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Transesterification of Vegetable Oil for Use as a Diesel Fuel
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by

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Abstract

The methyl ester of winter rape (MEWR) has been found to be a potentially useful substitute for diesel fuel. This paper discusses the procedure used to produce MEWR for use as a diesel fuel substitute. Reaction variables, rates, equipment and detailed procedures for making 756 l (200 gal) batches of MEWR. Systems for methanol and glycerol recovery are discussed. Zero profit economic data are also presented.

Introduction

The purpose of this paper is to report on the process for transesterification of vegetable oil to produce a more acceptable diesel fuel substitute. The use of vegetable oil as a fuel has been under study at Idaho since 1979. While short term tests are almost always positive; longer term tests with neat vegetable oil lead to severe engine deposits, ring sticking, injector coking and thickening of the lubricating oil.

Transesterification has shown good potential for reducing engine problems associated with vegetable oil fuels. Transesterification is the process of reacting a triglyceride with an alcohol in the presence of a catalyst to produce glycerol and fatty acid esters. The molecular weight of the ester molecule is roughly one-third that of a neat vegetable oil molecule, and the ester has a viscosity approximately twice that of diesel fuel. In contrast, raw vegetable oil has a viscosity of 10 to 20 times that of diesel fuel. Viscosity of the fuel is of prime concern because of its effect on spray patterns and deposit formation. Zhang et al. (1988) has shown that the methyl ester of high erucic acid rapeseed oil (MEWR) performs similarly to diesel in both short and long term engine tests. However, cloud points and pour points of vegetable oil esters are known to be much higher than diesel fuel and are much more susceptible to problems when used in cold weather.

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1. Identification of the process variables which affect the yield and conversion rate of winter rape vegetable oil to ester.

2. Identification of the equipment and procedures needed to successfully produce MEWR on a routine basis.

Review of Literature

Transesterification of vegetable oils with ethyl alcohol and methyl alcohol to produce ethyl esters and methyl esters has been the topic of several University of Idaho graduate thesis including Jo (1984), Madsen (1985), Melville (1987), Mosgrove (1987) and Caringal (1989). In each of these thesis, the literature reviews have reported investigations of the transesterification of several oils to produce methyl and ethyl esters; fish oil, soybean, sunflower, cottonseed, peanut and linseed oils have been transesterified. These transesterification studies have concentrated on optimizing the reaction variables of temperature, agitation time, ratio of alcohol to vegetable oil, and type of reaction rate enhancing agent.

Nye and Southwell (1983) investigated the effects of several important reaction parameters on the methanolysis of rapeseed oil. They reported finding successful conditions at room temperature by systematically optimizing the other operating variables. They identified the main variables as catalyst type, catalyst concentration, oil/alcohol ratio and stirring rate. They found that one percent NaOH or KOH was an effective reaction rate enhancer at room temperature; a 60-minute reaction time was allowed. It was determined that a 6:1 molar ratio of methanol to oil gave the best conversions. They also found that the rate of reaction is satisfactory if the stirring action is vigorous with some splashing.

Nye and Southwell (1983) extended their work on transesterification of rapeseed oil to produce the methyl ester in a bench-scale operation. They transesterified 25-liter (6.6 gallon) batches of oil in an enclosed stainless steel cylindrical drum which was equipped with a 4-inch diameter propeller driven by a 1/3 horsepower electric motor. Rapeseed oil was added to a solution of 1% sodium hydroxide (by weight relative to oil) dissolved in 6 molar equivalents of dry methanol. The solution was stirred with splashing for one hour at 24°C. The mixture was allowed to separate into two phases: one phase is rich in ester and unreacted methanol; the other phase is rich in glycerine and unreacted methanol. The ester phase was washed three times with water equal to half the volume of ester to remove methanol and potassium compounds. The ester was then dried over anhydrous calcium chloride and filtered.

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As the mixing rate is increased the initial rate of reaction increased. However, by 4 minutes the reaction rates were similar for all mixing rates and approximately the same final yields were obtained.

At this stage of the development, the emphasis was on production of the methyl ester. Consequently, the glycerine-rich phase was discarded; but the ester was purified by a washing process wherein water was allowed to percolate through the ester-rich phase until the methanol and potassium compounds were removed. As explained by Mosgrove (1987), each 151 l (40 gal) batch of MEWR required washing with water at the rate of 238 l/hr (63 gal/hr) for 8 hours. After washing, the MEWR was allowed to stand for 24 hours before transferring to a final storage tank.

Caringal (1989) performed considerable analytical work to define the details of the transesterification process. He obtained material balances for each step of the process and accounted for all materials entering and leaving each step of the process. He determined that the potassium leaving the ester phase in the wash water is in the form of a potassium soap. Caringal (1989) also proposed a process for recovering and purifying the by-product glycerine produced during the reaction. A flowsheet showing the transesterification process is shown as Figure 2.

Materials and Methods

Equipment

Extracting and Processing - All of the oil used in these studies has been extracted with a small oil extraction plant consisting of a mechanical screwpress manufactured by CeCoCo of Japan. The plant has a capacity of 45 kg per hour (100 lb per hour) and generates about 19 liters (5 gallons) of oil per hour. For a complete description of the process see Peterson et al. (1983).

The esterification plant, Figures 6 and 7, was designed for a 756 l (200 gallon) capacity. Typically 605 l (160 gallon) batches have been produced. The components of the system are: a 1096 l (290 gallon), cone bottom, cross-linked polyethylene tank purchased from Pasco Poly-Tank, Inc., Pasco, Washington; an R. S. Corcoran Co., New Lenox, IL, model 2000D Centrifugal pump (75 -95 l/min (20-25 gpm) capacity) compatible with methanol, vegetable oil, and KOH solutions, fluid viscosities from 0.65-55.0 centistokes and explosion proof; a 0.2 kW (1/4-hp) lab mixer with 3.4:1 gear reduction (1725 motor rpm and 514 rpm rotor rpm). The mixer should have an explosion proof motor. A 0.75 kW (1 horsepower) portable gear pump with totalizing meter is used to transfer the raw vegetable oil and the finished ester to the bulk storage tanks.

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purity. In our plant the mixing tank has been calibrated for measurement of the rape oil while a plastic barrel has been calibrated for measurement of the methanol.

3. Pump the clean raw, filtered rapeseed oil into the tank using the portable pump. If the pump has been used for another purpose flush it with about a gallon of rape oil before transferring the rape oil to the mixing tank.

4. Pump the methanol into the 190 l (50 gallon) tank using the system pump. Again some methanol should be used to flush pump and lines of contaminants and moisture.

5. Add the correct amount of KOH to the methanol, immediately cover and mix using the lab mixer until the KOH is completely dissolved (5 minutes is usually sufficient.) The barrel cover is designed with a slot for the mixer shaft. Provide good ventilation and use a ground strap to avoid sparks when pumping the methanol and during the first 30 minutes of mixing the vegetable oil/alcohol mixture.

6. Remove the lab mixer from the methanol and place into the ester mixing tank. Place the center of the shaft into the oil with the prop near the center of the tank.

7. With the mixer running, pump the methanol-KOH solution into the ester mixing tank using the system pump. The reaction will begin immediately and should be completed within 4 to 6 hours. The system pump is used intermittently during the reaction with the inlet tube near the tank bottom and the outlet near the top to aid the mixing process.

8. The order of the procedure is important. Having the rape oil pre-measured in the ester mixing tank minimizes the amount of time that methanol is evaporating (producing an explosion hazard) and eliminates the possibility of creating an excess ratio of KOH to rape oil during mixing. Likewise, complete dissolution of the KOH in the methanol prior to adding to the rape oil is important to prevent soap formation.

9. The reaction produces two liquids, methyl ester and it's by-product, glycerol. After 4 to 6 hours the mixer is removed from the tank. The system pump lines are removed. The tank is covered, and the mixture is allowed to settle for 12 hours or more to allow the glycerol to settle to the bottom.

PRODUCTION:

The equipment and procedures described above have been used to make seven, 605 l (160 gallon) batches of MEWR for a total of 4100 l (1100 gallons.) Additional quantities have been produced in smaller containers during the development of the procedures. Monitoring of the reaction rate in several of the batches produced results similar to that shown in Figure 8. Nearly complete conversion was reached in approximately one hour at room temperature. The ester thus produced has been used in the "Vegetable Oil for Diesel Fuel" project. The methyl ester is used as a replacement for diesel fuel in laboratory studies and in tractors used for field evaluation of problems associated with using the ester under actual field conditions. A 20 kW (27 hp) Satoh tractor has been powered with 100 percent MEWR since the spring of 1987. A second tractor, a John Deere 3150 of 75 kW (100 hp) size has been powered with a mixture of 50 percent methyl ester and 50 percent diesel for 2 years. Both tractors are performing satisfactorily to date.

Methanol Recovery:

Caringal (1989) reports that the methanol in the glycerol phase must be removed in order for the glycerol to be of commercial importance. He found that the glycerol has a methanol content of 30 percent by weight. This corresponded to almost 50 percent of the excess methanol. The simplest method of recovery is to vaporize the methanol. He found that distillate collected at 68°C to 120°C contained 99 percent by weight methanol.

Glycerol:

Caringal (1989) proposed two schemes for glycerol recovery. His process B, which was vacuum evaporation, was recommended. It had an 86.29 percent glycerol recovery and produced 98.2 percent glycerol. Caringal (1989) reported a price of $0.336 per kg ($0.74 per lb) for glycerol.

Economics:

Two U of I graduate students, Melville (1987) and Caringal (1989) have made zero profit analysis of the cost of MEWR.

Melville (1987) estimated the production cost of the ester as $0.31 per l ($1.18 per gallon) and $0.425 per l ($1.61 per gallon) for a COOP sized unit and Farm sized unit respectively. The farm size unit processed 78.6 t (86.7 tons) of seed per year producing nearly 34,000 l (9000 gallons) of ester per year (enough to meet the diesel demand of an average sized farm.) The COOP sized unit processed 1480 t (1,632 tons) of seed per year producing 655,000 l (173,000 gallons) of ester per year (enough to supply approximately 20 average sized farms.) Melville (1987)

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Ethyl Ester

Our on-going research involves the use of ethanol in the transesterification process. Ethanol is a better alcohol compared to methanol because ethanol is derived from agricultural products, is a renewable fuel, and is biologically more beneficial to the environment. Although the process of transforming vegetable oils is similar, research has shown that the optimum reaction conditions and procedures described in this paper for the production of methyl ester will not produce satisfactory results with the ethyl ester. Using the methyl ester process only 50 percent of the oil was was transformed to ester and no separation of the glycerol and ester phases was detected. Thus, a need to develop a new process for ethyl ester production was determined.

Literature and previous studies (Stern et al., 1986; Stern et al., 1985; Lago et al., 1985; and Kusy, 1982) indicate that for a successful tranesterification reaction, heating the mixture of oil, methanol and catalyst during the reaction was necessary to get satisfactory results. In earlier laboratory-scale ethyl ester production, this recommendation of heating the mixture was followed; however, we are concerned about additional cost and reduced energy efficiency.

More recent tests have been conducted without heating. Several different catalysts, various percentages of alcohol purity , and different molar ratios between ethanol and rapeseed oil have been used. Results have been mixed with regards to the completion of the reaction and the purities of the ethyl esters produced. As of this writing, ethyl esters have been produced with purities of over 95 percent (using HPLC analyses), and ester yields of more than 100 percent (using the input oil as the basis). Viscosity measurements on the ethyl esters show levels comparable to that of the methyl esters. Cloud point and pour point analyses reveal that the ethyl esters have generally lower cloud and pour point compared to the methyl esters. This is a definite advantage since the pour point of methyl esters was a concern for use in engines and a search for a usable pour point depressant has been in progress.

Although conditions for a successful transesterification process have been identified, there are still problems to be overcome in the optimization of ester ester production. Satisfactory yields have been produced,; but, as yet we cannot recommend the whole process. Additional research will be needed to produce quantities of ethyl ester similar to that of methyl ester at room temperature.

Disclaimer Statement

This report contains a summary of research results. This is not to be construed as a recommendation for the use of any

Madsen, Jeff. 1985. Fuel Performance and Reaction Rate
     Characterization of Esters from Vegetable Oils, An unpublished
     M.S. thesis, Department of Chemical Engineering, University of
     Idaho, Moscow, Idaho.

Melville, D. E. 1987. Process Scale-Up and Long Term Engine
     Testing of Rapeseed Methyl Ester for a Diesel Fuel Substitute.
     An unpublished M. S. thesis, Department of Chemical
     Engineering, University of Idaho, Moscow, Idaho.

Mills, G. and A. Howard. 1983. Preliminary Investigation of
     Polynuclear Aromatic Hydrocarbon Emissions from a Diesel
     Engine Operating on Vegetable Oil-Based Alternative Fuels,
     Journal of the Institute of Energy, volume 131.

Mittelbach, M., P. Tritthart and H. Junek. 1985. Diesel Fuel
     Derived from Vegetable Oils, II: Emission Tests Using Rape Oil
     Methyl Ester. Energy in Agriculture 4:207-215.

Mosgrove, V. L. 1987. Preparation and Performance of Rapeseed Oil
     Fatty Ester as Diesel Fuels. An unpublished M. S. thesis,
     Department of Chemical Engineering, University of Idaho,
     Moscow, Idaho.

Nye, M. J. and Southwell, P. H. 1983. Esters from Rapeseed Oil as
     Diesel Fuel, proceedings from the Vegetable Oil as Diesel Fuel
     Seminar III, Northern Agricultural Energy Center, Peoria, IL.

Peterson, C. L., D. L. Auld and J. C. Thompson. 1983. Experiments
     with Vegetable oil Expression. Transactions of the ASAE
     26(5):1298-1302.

Romano, S. 1982. Vegetable Oils - A New Alternative. Vegetable
     Oil Fuels, Proceedings of the International Conference on
     Plant and Vegetable Oils, ASAE Publication 4-82, ASAE, St.
     Joseph, MI 49085.

Stern, R., G. Hillion, P. Gateau and J. C. Guibet, 1986.
     Preparation of Methyl and Ethyl Esters from Crude Vegetable
     Oils and Soapstone. In Proceedings of the World Conference on
     Emerging Technol. Fats, Oils Ind. (A. Richard Baldwin, Editor)
     American Oil Chemists Society, Champaign, Il. pp. 420-422.

Stern, R., G. Hillion, P. Gateau and J. C. Guibet, 1985. New
     Process for the Fabrication of Ethyl Esters from Crude
     Vegetable Oils and Hydrated Ethyl Alcohol. Biomass Energy,
     Comm. Eur. Communities [Rep.] Eur, Eur 10024. pp. 147-154.

Zhang, Q. 1988. The Effects of Methyl Ester of Winter Rapeseed
     Oil on Diesel Engine Durability. An unpublished M. S. thesis,
     Department of Agricultural Engineering, University of Idaho,
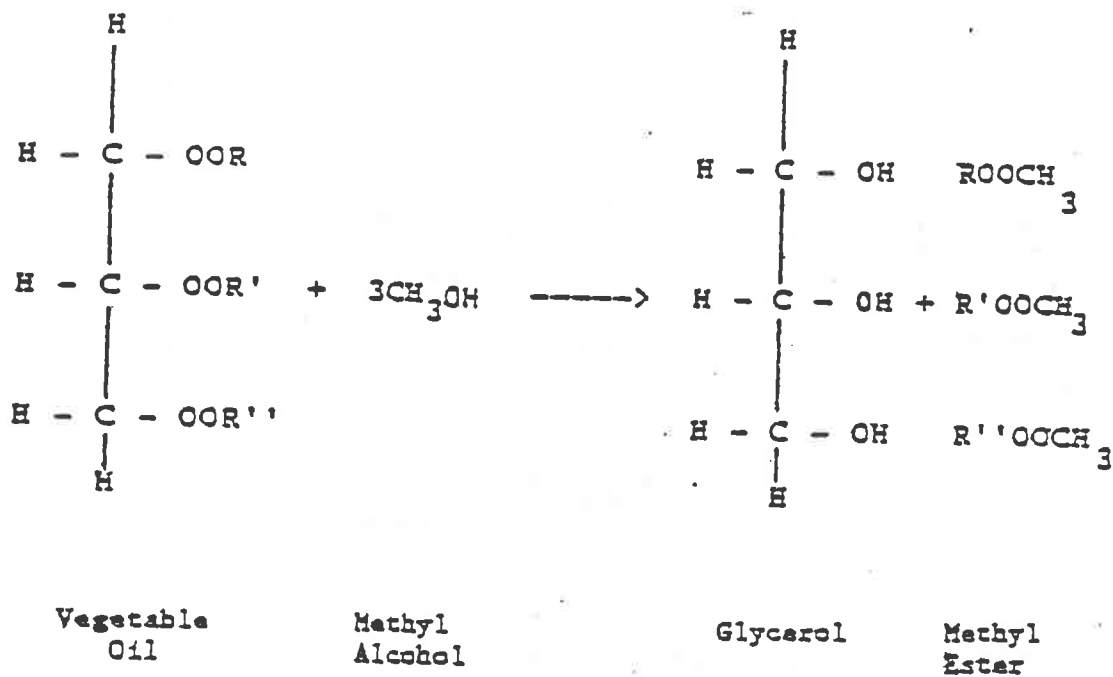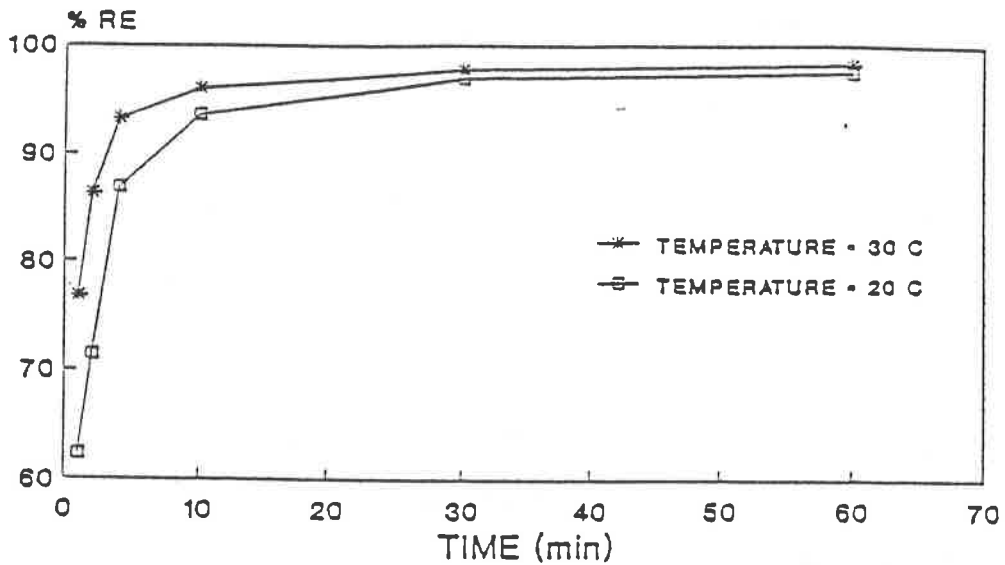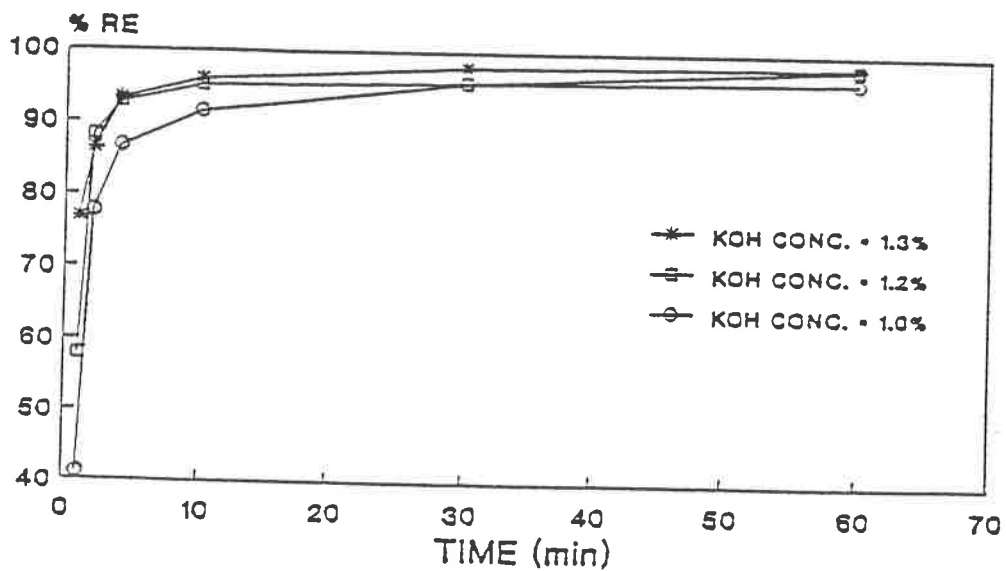   Moscow, Idaho.

$$H$$

$$\begin{array}{ccc}
& H & \\
& | & \\
H - C - OOR & & H - C - OH \quad ROOCH_3 \\
| & & | \\
H - C - OOR' & + \; 3CH_3OH \; \longrightarrow \; H - C - OH \; + \; R'OOCH_3 \\
| & & | \\
H - C - OOR'' & & H - C - OH \quad R''OOCH_3 \\
| & & | \\
H & & H
\end{array}$$

| Vegetable | Methyl | Glycerol | Methyl |
| Oil | Alcohol | | Ester |

Figure 1. Vegetable Oil Transesterification

Figure 3. Rate of ester conversion versus temperature, Madsen (1985).

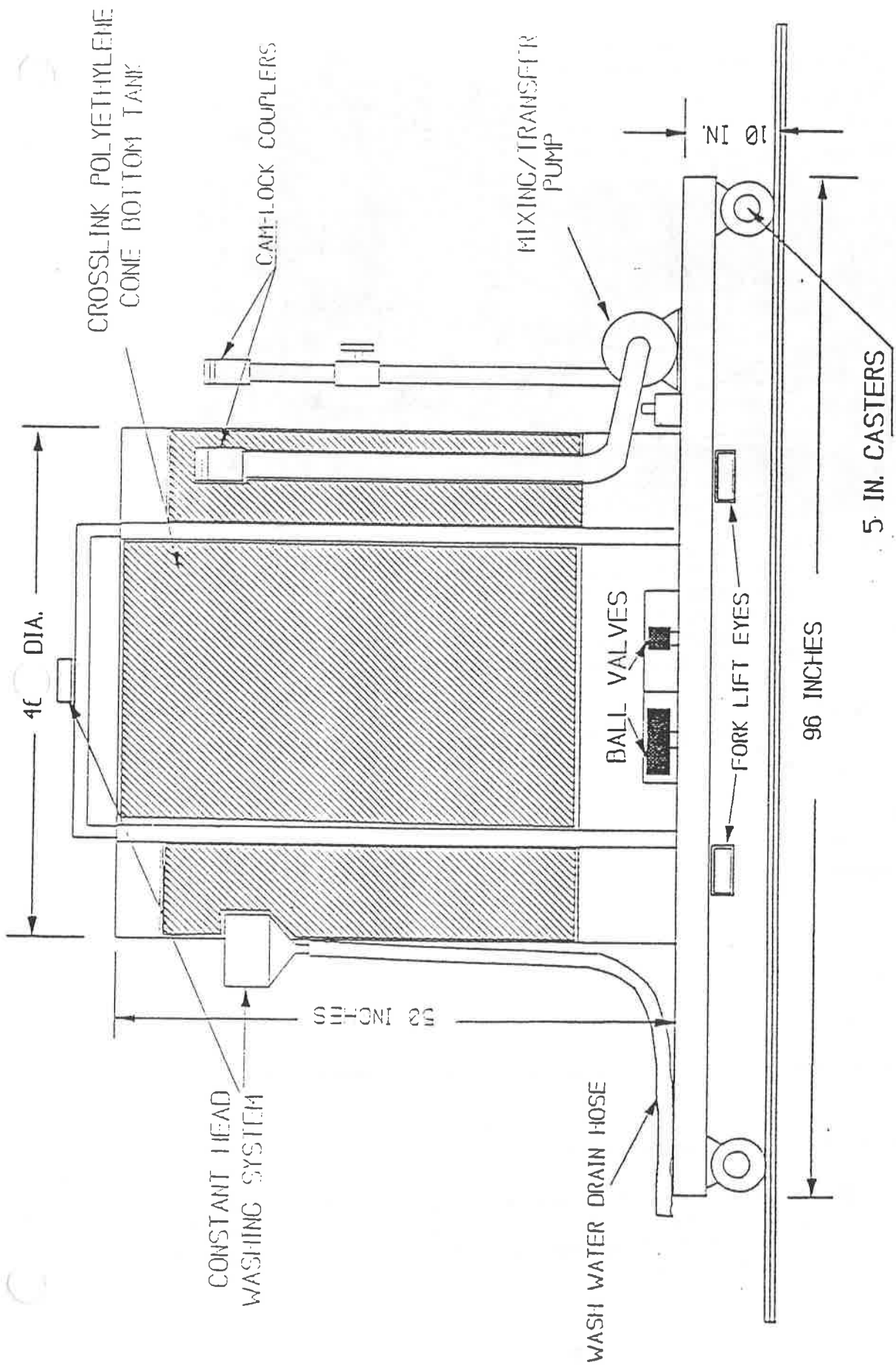Figure 4. Rate of ester conversion versus catalyst concentration, Madsen (1985).

Figure 6. Schematic of the rape oil transesterification plant.

CROSSLINK POLYETHYLENE CONE BOTTOM TANK

CAM-LOCK COUPLERS

MIXING/TRANSFER PUMP

BALL VALVES

FORK LIFT EYES

CONSTANT HEAD WASHING SYSTEM

WASH WATER DRAIN HOSE

10 IN.

5 IN. CASTERS

96 INCHES

52 INCHES

46 DIA.