TRANSESTERIFICATION PROCESS TO MANUFACTURE ETHYL ESTER OF RAPE OIL

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ABSTRACT

A process for the production of the ethyl ester of winter rape [EEWR] for use as a biodiesel fuel has been studied. The essential part of the process is the transesterification of rape oil with ethanol, in the presence of a catalyst, to yield the ethyl ester of rape oil as a product and glycerin as a by-product. Experiments have been performed to determine the optimum conditions for the preparation of EEWR. The process variables were: 1) temperature, 2) catalyst, 3) rate of agitation, 4) water content of the alcohol used, and 5) the amount of excess alcohol used. The optimum conditions were: 1) room temperature, 2) 0.5% sodium methoxide or 1% potassium hydroxide catalyst by weight of rapeseed oil, 3) extremely vigorous agitation with some splashing during the initial phase of the reaction and agitation was not necessary after the reaction mixture became homogeneous, 4) absolute ethanol was necessary for high conversion, and 5) 50% excess ethanol with $NaOCH_3$ or 100% excess with KOH gave a maximum conversion. Viscosity, cloud point and pour point of the EEWR were measured. A preliminary break-even cost for the commercial production of EEWR was found to be $0.55/liter [$2.08/U.S. gallon].

INTRODUCTION

Background

Vegetable oils have attracted attention as a potential renewable resource for the production of an alternative for petroleum-based diesel fuel. Various products derived from vegetable oils have been proposed as an alternative fuel for diesel engines, including neat vegetable oil, mixtures of vegetable oil with petroleum diesel fuel, and alcohol esters of vegetable oils. Alcohol esters of vegetable oils appear to be the most promising alternative. Vegetable oils are triglycerides [glycerin esters] of fatty acids; alcohol esters of fatty acids have been prepared by the transesterification of the glycerides, wherein linear, monohydroxy alcohols react with vegetable oils in the presence of a catalyst to produce alcohol esters of vegetable oils [AEVO] and glycerin as a by-product (Fig. 1). AEVO when used as an alternative diesel fuel has been identified as a "biodiesel".

Detailed literature reviews concerning the production and use of AEVO have been given by Peterson et al. (1991) and Bam (1991). Previous publications reported the use of methyl, ethyl, and butyl alcohols for the transesterification of rape oil, sunflower oil, cottonseed oil, peanut oil, soybean oil, and palm oil to produce methyl, ethyl, and butyl esters. The transesterifications were enhanced by the use of potassium hydroxide, sodium hydroxide, sodium methoxide, or sodium ethoxide as a catalyst. Important reaction parameters for the transesterifications are: 1) ratio of alcohol to vegetable oil, 2) temperature, 3) rate of agitation, and 4) amount of water present in reaction mixture.

AEVO has a viscosity approximately twice that of diesel fuel. Viscosity is of prime concern because of its effects on spray patterns and deposit formation. AEVO performs similarly to diesel in both short- and long-term engine tests (Fig. 2) while the raw vegetable oil develops severe injector fouling after 200 hours of operation.

Alcohol esters of fatty acids have surprisingly good emission characteristics; the emissions of methyl esters of winter rape [MEWR] gave significantly lower total particulates and lower polynuclear aromatic hydrocarbons than #2 diesel fuel. However, combustion of MEWR gave higher levels of NO_x and aldehyde emissions than did #2 diesel fuel. Additional tests of emissions from biodiesel fuels are needed to enhance their commercialization.

The use of neat vegetable oil, mixtures of vegetable oil and other components, and alcohol esters of vegetable oils [AEVO] has been under study at the University of Idaho since 1979. Peterson et al. (1991) have given a complete description of the process for the production of the methyl ester of winter rape [MEWR]. MEWR has been manufactured in a 756-liter [200 - U.S. gallons] batch pilot plant scale (Fig. 3) using potassium hydroxide as a catalyst. The MEWR biodiesel product has been used as a replacement for diesel fuel in laboratory studies and in tractors using the ester under actual field conditions. A 20 KW (27 hp) Satoh tractor has been powered with 100% MEWR biodiesel since the spring of 1987. The tractor has been performing satisfactorily to date. A preliminary economic analysis of the commercial production of MEWR showed a break-even cost of $0.49/liter [$1.85/U.S. gallon). Costs are in 1991 U.S. dollars.

Research at the University of Idaho has been focused on alcohol esters of vegetable oils because vegetable oils are a renewable energy resource. Earlier work has concentrated on methyl esters. The next logical step is the use of ethanol rather than methanol and consequently produce the ethyl ester of vegetable oils. Ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols. Consequently, a process for the production of the ethyl ester of winter rape [EEWR] for use as a biodiesel fuel has been studied. The process system which has been studied is similar

to the process for production of MEWR as shown in Figs. 1 and 3 except ethanol was used instead of methanol and catalysts other than KOH as well as KOH were tested.

Objective

Optimum conditions for the transesterification of rape oil to produce EEWR were determined which yielded a maximum conversion of rape oil to the ethyl ester. The variables were: 1) Temperature of reaction; 2) Catalyst; 3) Rate of agitation of reaction mixture; 4) Water content of alcohol (ethanol); and 5) Amount of excess alcohol.

METHODS

Materials

The rapeseed oil used for the experiments was extracted from Bridger rapeseed; Bridger is a winter variety of rape. This oil has a high level of erucic acid (53.2%). Extraction of the oil from the rapeseed (Fig. 3) was done by the Department of Agricultural Engineering at the University of Idaho (Peterson et al. 1983). A Cecoco oil expeller press with an extraction efficiency of approximately 80% was an integral part of their process. The automated and instrumented system was equipped with a seed preheater-auger, seed bin, meal auger, and oil pump. Reagent grade absolute ethanol was used. Potassium hydroxide pellets with an assay of 85% were purchased from EM Science Company; Fisher Scientific Company provided the purified, dry sodium methoxide powder; sodium ethoxide was provided by Aldrich Chemical Company; and potassium methoxide was a product from Aldrich Chemical Company.

Fractional Factorial Experimental Design

A fractional, factorial experimental design was used to determine the optimum values of temperature, degree of agitation, type of catalyst, and water content of ethanol used. A 2^{4-1} fractional, factorial design was chosen for this purpose. Using a 2^{4-1} design, four variables were studied at two levels by performing eight experiments ($2^{4-1} = 8$). The fractional, factorial design contains three quantitative variables - temperature, agitation, and water content of ethanol - and one qualitative variable - catalyst. The response is degree of conversion of rape oil to ethyl ester. The design matrix (Table 1) shows the two levels of the variables and the response. Table 1 shows the recorded data with the levels coded so that a minus one (-1) represents the low level and a plus one (+1) represents the high level. The catalyst chosen for the lower level was sodium ethoxide and potassium hydroxide was chosen for the higher level.

The levels which were chosen for the various variables in this study were based on previous experiments and practical considerations. The low level of temperature was chosen as room temperature and the high level was chosen slightly higher below the boiling point of 190 proof ethanol. The lower level of ethanol chosen was 190 proof (five wt percent water); the higher level was 200 proof (zero wt percent water). The lower level of agitation was a gentle agitation and the higher level of agitation was an extremely vigorous agitation with some splashing.

Table I. Design Matrix for the Experimental Design

Parameters			Levels	
1 - Agitation			High (+1)	Low (-1)
2 - Temperature			75 C	30 C
3 - Catalyst			KOH	$NaOC_2H_5$
4 - Ethanol			200 proof	190 proof

Expt No.	Parameters 1 2 3 4	% Conversion
1	-1 -1 -1 -1	51
2	+1 -1 -1 +1	98
3	-1 +1 -1 +1	81.5
4	+1 +1 -1 -1	45
5	-1 -1 +1 +1	91.7
6	+1 -1 +1 -1	29
7	-1 +1 +1 -1	77.8
8	+1 +1 +1 +1	100

Experimental Setup and Procedure

Three operations were studied in the experimental work which was performed. These are shown in Figure 3; they are: 1) transesterification, 2) phase separation, and 3) washing. Figure 1 shows the tranesterification; in this study ethanol, in presence of a catalyst, instead of methanol was used and ethyl ester was produced. After the reaction was complete, the reaction products separated into two layers; the ester product formed the upper layer and the by-product glycerin formed the lower layer. The residual catalyst and unreacted excess alcohol were distributed between the two phases. After separation of the phases, the catalyst and alcohol were washed from the ester with water.

Transesterification

The transesterification experiments were performed in conical flasks using 250 g of rapeseed oil. Catalysts were 2.5 g (1% by weight of the oil) of potassium hydroxide or 1.25 g (0.5% by weight of oil) of sodium ethoxide The catalyst was first dissolved in 72 g of ethanol which represented a 100% excess of the stoichiometric amount required for the transesterification. It was necessary to heat the ethanol slightly with stirring to completely dissolve the catalyst The ethanol and dissolved catalyst were then added to the oil and stirring was begun. Samples of approximately 3-4 ml of the reaction mixture were pipetted out at 1, 30, 60, and 120 minutes respectively. The reaction was arrested in the samples by adding one or two drops of water. The samples were analyzed to determine the degree of completion of the reaction .

Additional experiments were conducted to study the effects of temperature and sodium methoxide and potassium methoxide catalysts on ester yields. Experiments were also performed to determine ester yields using the stoichiometric amount and amounts of alcohol equal to 50%, 75%, and 100% excess.

Phase separation

After 120 minutes of reaction time, the reaction was stopped and the reaction mixture was allowed to stand overnight while phase separations occurred. The ester phase was then decanted from the equilibrium mixture.

Washing

Excess alcohol and residual catalyst were washed from the ester with water. The ester phase was placed in a glass column 1.26 cm in diameter and 100 cm in length. Water was sprayed into the top of the column at a low velocity. The excess alcohol and catalyst were removed by the water as it percolated through the column. During the washing, some of the ester formed an emulsion with the water; a time of 24-48 hours was required for the water phase containing alcohol, catalyst, and emulsified ester to settle and the ester phase to become clear.

Analyses

The analyses have been described by Bam (1991). High Performance Liquid Chromatography (HPLC) was used to determine the composition of the reaction mixture and the ester conversion. The composition of the ester was determined by Gas Chromatography (GC). Viscosity measurements of the ester were made by following ASTM standards (ASTM D445 or IP 71). The ester was analyzed for cloud and pour points by following ASTM Standards D2500-81 and D97, respectively.

RESULTS AND DISCUSSION

Statistical Analysis of Experimental Design

The results obtained from the eight experiments performed according to the fractional factorial design (Table 1) were analyzed using Statistical Analysies System (SAS). The results of this analysis were used to develop an equation which shows the relationships between degrees of conversion, rate of agitation, temperature, water content of ethanol, and catalyst.

$$CONV = 71.75 - 3.75(A) + 4.325(T) + 21.05(ALC) + 9.95(T)(C) - 6.37(T)(ALC) \qquad (1)$$

where A = rate of agitation; T = temperature; ALC = water content of alcohol; C = catalyst; and CONV = percentage conversion of oil to ester.

In this equation, the values of A are either -1 (low agitation) or +1 (high agitation); values of T are either -1 (30C) or +1 (75C); values of ALC are either -1 (190 proof) or +1 (200 proof); values of C are either -1 (NaOC$_2$H$_5$) or +1 (KOH). For example, with high agitation, with temperature = 75C, using NaOC$_2$H$_5$ as catalyst, and 190 proof ethanol,

$$CONV = 71.75 - 3.75(+1) + 4.325(+1) + 21.05(-1) + 9.95 [(+1)(-1)] - 6.375[(+1)(-1)]$$
$$= 47.7\%$$

Inspection of Equation (1) shows that water content of alcohol is the most important independent factor affecting degree of conversion and that increasing water content (lowering proof) decreases degree of conversion. Further inspection shows that the interaction between temperature and catalyst and the

interaction between temperature and water constant of alcohol are significant.

A matrix was designed which contained sodium methoxide and potassium methoxide in place of potassium hydroxide and sodium ethoxide as shown in Table 1. The conversions obtained were approximately the same for all catalysts except potassium methoxide. The conversion obtained with potassium methoxide was significantly lower.

Phase separation was also treated as the dependent variable as a function of agitation, temperature, catalyst and water content of alcohol. The type of catalyst used was an important variable affecting the separation of the ester phase from the glycerin phase. Temperature, alcohol, and the interaction between temperature and alcohol also had significant effects on phase separation.

Optimum Conditions for Ethyl Ester Preparation

Transesterification

Temperature had no detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion. It is believed the cost of energy for heating would exceed the value of time saved by using higher temperatures. Therefore, room temperature is considered to be the optimum temperature for conversion.

A high degree of conversion could be obtained only if the oil and alcohol phases have been blended into one homogeneous phase. This requires extremely vigorous agitation with some splashing at the start of the reaction. When the reaction mixture is homogeneous, the conversion and time to reach maximum conversion are independent of agitation.

The presence of water in the reaction mixture markedly reduces the conversion of oil to ester (see Equation 1). 200 proof ethanol must be used in order to obtain a high degree of conversion. The experiments in which different amounts of excess alcohol were used in the reaction mixture showed that an amount in 50% excess of the stoichiometric ratio gave a high conversion when sodium methoxide was the catalyst. Potassium hydroxide catalyst required 100% excess alcohol to achieve similar conversion and phase separation from the glycerin.

Although SAS indicated sodium ethoxide, sodium methoxide, and potassium hydroxide all gave good conversions during transesterification, sodium methoxide was chosen as the most promising catalyst due to phase separation considerations described below. Experiments were performed in which the concentration of sodium methoxide varied from 0.3% to 0.5% by weight of rapeseed oil used. Conversion was maximum for 0 5% concentration of catalyst.

Phase Separation

The type of catalyst used during the transesterification has an important effect on the subsequent phase separation. Phase separation was erratic and dependent upon the amount of excess alcohol present in the case of potassium hydroxide. No phase separation occurred when potassium methoxide was used. When sodium methoxide or sodium ethoxide was used, separation was good; however, sodium methoxide was judged to give the better result.

The impact of variables other than catalyst and excess alcohol on phase separation was considered minor relative to their impact on transesterification.

Washing

During the washing of the ester phase care must be taken to add water slowly in a fine spray. Agitation of the ester with the flow of water caused a loss of as much as 18% of the ester due to the formation of an emulsion.

The importance of washing is the removal of residual catalyst from the ester. The effluent wash water was monitored for sodium content and washing continued until the sodium content of the effluent was the same as the sodium content of the entering wash water. Complete removal of catalyst from the ester was assured by determining the amount of sodium in the glycerin phase and the total sodium removal from the ester phase. The sum of these accounted for all of the sodium entering the reaction as a constituent of the catalyst.

Physical Properties of EEWR

The measured viscosity of the ethyl ester was 7.0 centistokes at 25C. The viscosity of the rapeseed methyl ester is 6 cs at 40C and 2.39 cs at 100C; the viscosity of #2 diesel is 3.2 cs at 40C and 1.26 cs at 100C. The cloud and pour points of the ethyl ester was found to be -7C and -16C, respectively.

Preliminary Economic Evaluation Between Methyl and Ethyl Esters

The economic viability of the rapeseed ethyl esters was compared to that of methyl esters. This was done by comparing the breakeven cost of methyl ester with that of ethyl ester. Breakeven costs were found by determining the sales value of product which would be required to operate a manufacturing facility at zero profit. At zero profit the total of all annual costs equals the sales value. In the comparison made in this study, annual costs were separated into raw material costs and all other costs which were identified as processing costs. Figure 4 shows the breakeven cost for four different situations. These are 1) methyl ester using KOH as catalyst and methyl alcohol, 2) ethyl ester using KOH as catalyst and denatured 200 proof-ethanol, 3) ethyl ester using sodium methoxide as catalyst and denatured 200 proof ethanol, and 4) ethyl ester using sodium methoxide as catalyst and 200 proof absolute alcohol. It can be noted that oil is the major cost in all cases. Raw material costs were based on a rapeseed oil cost of $0.44/kg [$0.20/lb]. The breakeven cost for methyl ester is $1.85/U.S. gallon and the maximum cost for ethyl ester is $2.39/U.S. gallon.

CONCLUSIONS

Rapeseed oil ethyl ester can be made successfully under the following conditions for transesterification: 1) Room temperature; 2) 0.5% sodium methoxide catalyst based on weight of rapeseed oil and 50% excess of the stoichiometric amount of required 200 proof alcohol; or 3) 1.0% potassium hydroxide catalyst and 100% excess of the stoiciometric amount of 200 proof alcohol; 4) Extremely vigorous agitation with a little splashing until the reaction mixture becomes homogeneous.

Since the ester has an extremely high tendency to form an emulsion on contact with water, care must be taken to maintain low levels of agitation during washing.

The economic viability can be significantly improved if lower valued oil feedstocks can be obtained. Waste animal fats from meat processing facilities, waste frying oils from French fried potatoes and other food frying operations, and low-grade residue oils from food grade oil crushing and refining plants could be

substituted for the rapeseed oil used in this study. The ethanol must be moisture free, but can be denatured with small amounts of gasoline

ACKNOWLEDGEMENTS

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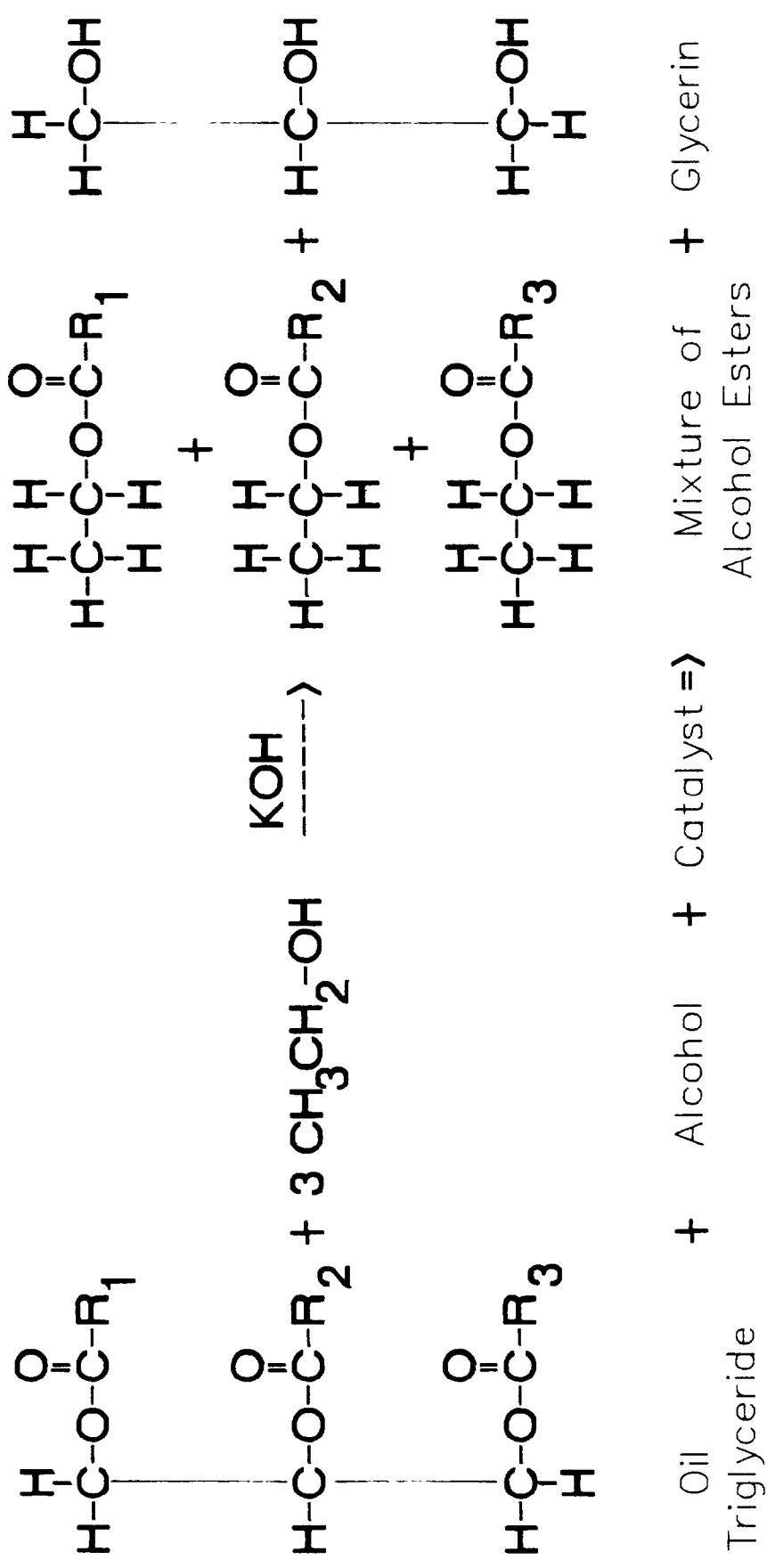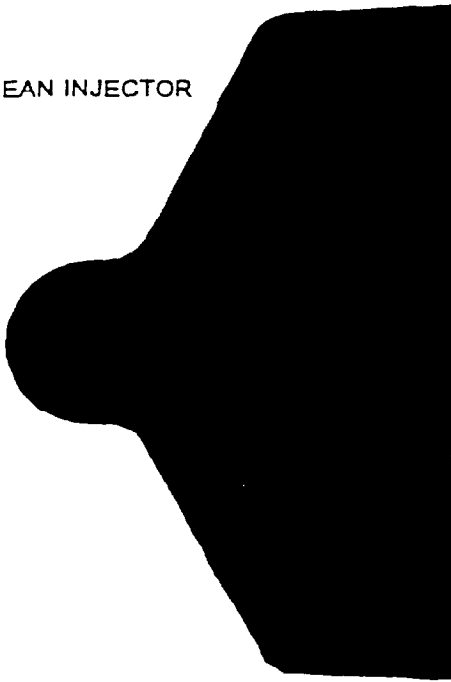
Figure 1. Transesterification Chemistry
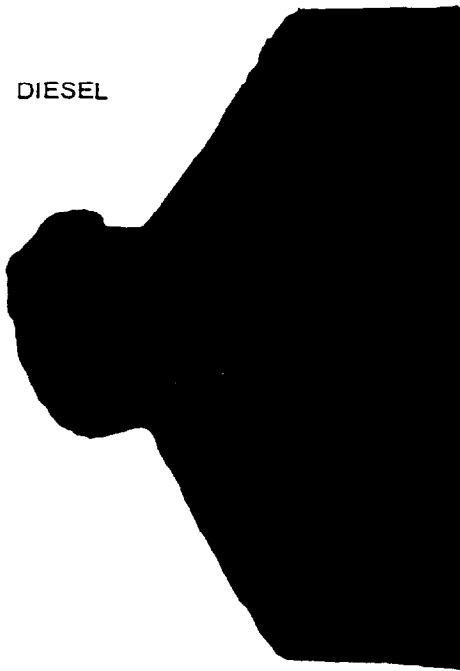
CLEAN INJECTOR

200 HOURS
50:50 BLEND
RAPESEED OIL
#2 DIESEL

200 HOUR EMA ENGINE TEST CYCLE

#2 DIESEL

RAPESEED
METHYL ESTER

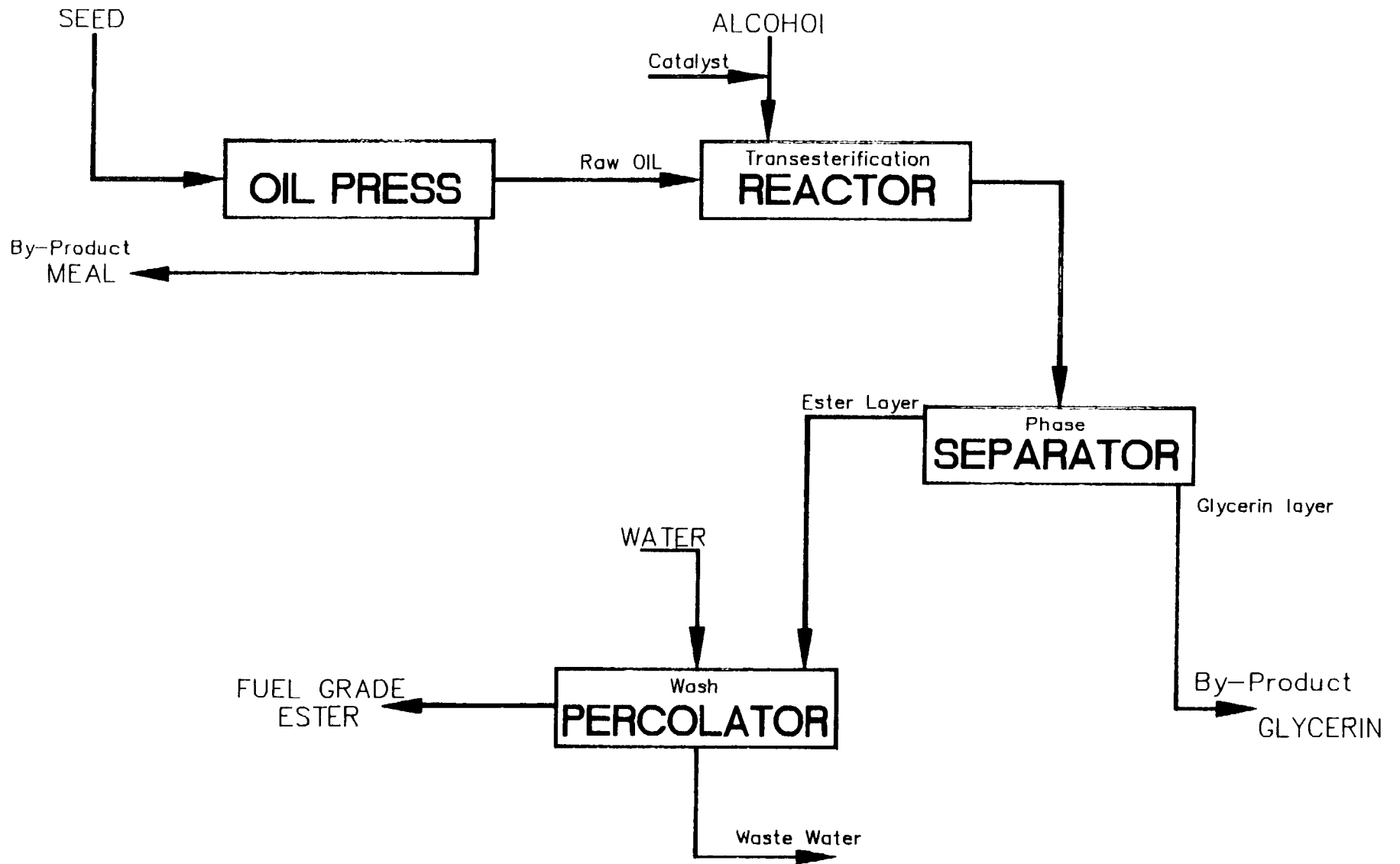Figure 2. Injector nozzles: 200 hour EMA Engine Test Cycle
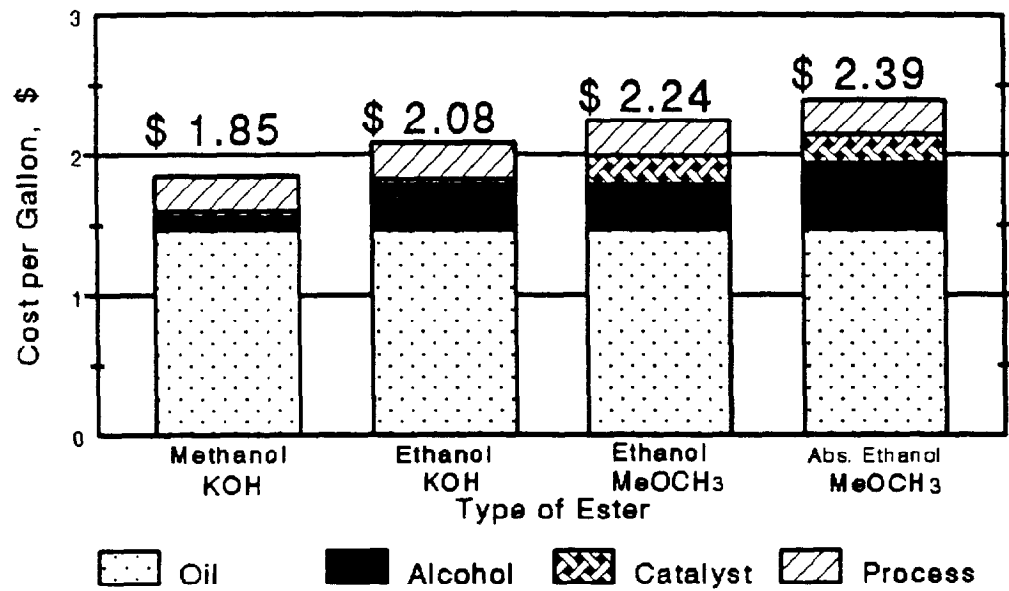
Figure 3. Biodesel Transesterification Process Flowsheet

Figure 4. Cost of Ester Production