

COMPARISON OF TOTAL ENERGY CONSUMPTION NECESSARY FOR SUBCRITICAL AND SUPERCRITICAL SYNTHESIS OF BIODIESEL

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1. INTRODUCTION

Mixture of fatty acid methyl esters (FAME or biodiesel) is today in use as non-toxic fuel obtained from different and renewable sources. For FAME synthesis the homogeneous (alkaline or acid catalyzed), non-catalytic supercritical, and recently the heterogeneous process at higher temperature and pressure have applied. However, majority of industrial plant are designed and today operate on the basis of alkaline technology. Knowing all drawback of alkaline process many investigation have started with a goal to develop new technology for FAME production (supercritical non-catalytic synthesis or subcritical condition with heterogeneous catalyst).

Analysis of several different schemes for FAME production which are based on application of higher pressure and temperature (subcritical and supercritical conditions; catalytic or non-catalytic synthesis) was realized in this study. The mass and energy balances of FAME synthesis were calculated using ASPEN Plus software assuming different degree of conversion of vegetable oil (triglycerides).

2. MATERIALS AND METHODS

2.1. Process simulation

The process simulation software ASPEN Plus[®] v2006 was used to carry out the simulations. The procedures for process simulations consist in defining components, defining appropriate thermodynamical model, the required equipment and operating conditions. The mass and energy balances for each unit, as well as operating conditions, were obtained. The pressure drop in different equipments obviously exists but in this study it was neglected.

2.1.1. Key component

Since oleic acid is the major fatty acid in most vegetable oils (canola, rapeseed and sunflower oil) and the component for which there is available thermodynamic properties in the literature, it was chosen that ester of glycerol and oleic acid represents the key component in the simulation (trioleine). Accordingly, methyl oleate (C₁₉H₃₆O₂) was taken as the resulting product of methanolysis or the formal representative of FAME or biodiesel. The plant capacity was calculated for FAME annual production of 10,000 tones and 7900h/year. In each simulation the resident time of reaction mixture in reactor for FAME synthesis was kept constant as well as the purity of final product.

2.1.2. Thermodynamic models and kinetic data

The main process units of biodiesel production in the high pressure operating regime are: pumps for pressurizing methanol and triglyceride, mixers, the heat exchangers for achieving the high temperature or supercritical state of reaction mixture, chemical reactor and depressurising valves. In the lower pressure and temperature operating regime the main equipments are: distillation columns for separating and recycling the large excess of methanol used in synthesis and distillation columns for purification the final products (FAME and glycerol) to desired characteristics defined by corresponding standards.

The rate constant for the first-order irreversible reaction of methanolysis under supercritical condition used for calculation the volume of reactor is based on data recently published in literature¹ ($7.300 \cdot 10^{-4}$ at 280°C and 28 MPa). For other temperature and pressure the reaction rate constant was calculated on the basis of activation energy which is for subcritical condition 11.2 kJ/mol and for supercritical condition 56.0 kJ/mol , while $-206 \text{ cm}^3/\text{mol}$ is also used as corresponding activation volume necessary for identifying the influence of pressure on reaction rate constant¹.

The thermodynamic behaviour at high pressures and temperatures of the system methanol-trioleine was correlated with RK Aspen EOS².

After the chemical reactor, the pressure and temperature must be decreased; since glycerol are not stable and could be thermally decomposed. Low-pressure section includes as main units: distillation column for separating excess of methanol, mixing device for mixing the recycle and fresh methanol with oil phase, gravitational separator for separation FAME and glycerol and distillation columns for FAME and glycerol purification. Therefore, for separation process of FAME and glycerol and their purification a different thermodynamical model must be and was employed in this study. The UNIQUAC and UNIFAC-LL models were used to simulate the performance of equipment operating at near atmospheric pressure.

2.2. Process design

Biodiesel is currently defined in the European Union by technical regulation EN 14214:2003 or in the USA by ASTM 6751-07. In order to produce biodiesel which fulfils these regulations it is necessary to follow a strict procedure for used raw material, working or reaction conditions and use of different type of catalyst. Among several steps in FAME synthesis the extent of chemical reaction and total conversion of triglyceride is most important determining downstream phases in biodiesel production (FAME and glycerol purification).

Four different continuous processes (I-IV) were defined and analyzed which could be realized at subcritical or supercritical condition. For all proposed schemes (I-IV), the same molar ratio (42:1) of methanol and sunflower oil (represented by triolein¹) was used. Other parameters and information used in these simulations for different production scheme are given in **Table 1**. The last simulation (V) was done assuming that 97 mass% conversion of triglyceride could be obtained in the presence of heterogeneous catalyst³ at same P and T previously used in simulation IV but with smaller methanol:oil ratio (15:1). Other process parameters for all simulation are shown in **Table 1**.

Table 1. Process parameter used in different simulation scheme

Simulation	I	II	III	IV	V
	Subcritical	Supercritical	Subcritical and Catalyst	Supercritical	Subcritical and Catalyst
Temperature, °C	150	280	150	280	150
Pressure, MPa	20	28	20	35	20
Oil to methanol ratio	1:42	1:42	1:42	1:42	1:15
Yield, mass%	80.9	97.0	97.0	100.0	97.0
Reaction rate constant, 1/s	$3.634 \cdot 10^{-4}$	$7.300 \cdot 10^{-4}$	$7.300 \cdot 10^{-4}$	$1.056 \cdot 10^{-3}$	$7.300 \cdot 10^{-4}$
Relative volume of reactor (ratio V/V_{IV})	0.47	1.03	0.39	1	0.23

The main attention in these simulations was paid to:

- a) Determining the rate of reaction under different working condition^{1,2};
- b) Calculating of total energy consumption for biodiesel synthesis, and
- c) Calculating the energy consumption for different steps of subcritical and supercritical processes (heating of reaction mixture; pumping to desired pressure; recovery of methanol; purification of FAME and glycerol; and recuperation of energy - cases II and III).

The process flowsheets and the main streams for all processes are presented in **Fig. 1**.

2.2.1. Description of process flowsheet

2.2.1.1. Methanolysis

The plug flow reactor (a heat exchanger type) was selected as the best type of reactor for performing the methanolysis of triglycerides. Fresh methanol feed (stream 101) is mixed with recycled methanol (stream 301-A) and stream 101-A is pumped into the reactor R-201 along with stream of vegetable oil (i.e. triglycerides which are represented in this simulation by key component - trioleine) (stream 102). Reaction mixture of trioleine and methanol (stream 103) is heated up in heat exchanger E-201 using heating oil (stream 605). The reactor operating conditions (P, T) directly influence degree of conversion of triglycerides. After the reaction the products (stream 202) are cooled down (E-202) and depressurized in three steps passing through the valves (V-201, V-202 and V-203). This part of the process is conducted at high pressure and therefore RK-ASPEN EOS was used for calculation necessary parameters of reaction mixture. All simulation (degree of conversion of triglyceride) was realized on the basis of constant value of resident time in reactor (1.24 h) while required kinetic constant was used or calculated on the basis of literature data^{1,2}.

2.2.1.2. Methanol recycling

Required molar ratio methanol to oil (42:1) for SCA is much higher than theoretical needs according to the overall stoichiometry of reaction between methanol and trioleine (3:1). For this reason after the reaction step, the excess of methanol has to be recycled into the process in distillation column T-301, where methanol is the top product with almost 100 % purity (stream 301). Column T-301 has four theoretical stages and operates with reflux ratio 2.

2.2.1.3. FAME purification

Bottom product from distillation column T-301 (stream 302) is a mixture, which consists mainly of FAME (methyl oleate), glycerol, trioleate and methanol, which are treated further in gravity separator (D-301). After separation, upper portion (stream 303) which contains mainly methyl oleate (>95.3 mass%), methanol and a small amount of glycerol and trioleate is separated in distillation column T-401 where FAME is finally obtained as liquid product from distillate (stream 401-A).

Distillation columns (T-301, T-401 and T-501) operate under vacuum in order to achieve low temperatures profiles in the column and prevent degradation of FAME and glycerol. Obtained FAME is a mixture of methyl oleate, trioleine, methanol and glycerol (**Table 2**). Column T-401 has five theoretical stages and reflux ratio 2.

2.2.1.4. Glycerol purification

In order to get high quality glycerol and makes biodiesel production more economical a separation of glycerol fraction must be realized using distillation column T-501. Therefore it is necessary to remove the excess of methanol which is present in stream 304. The composition of bottom product (stream 502) of distillation column T-501 is almost pure glycerol (**Table 2**). Glycerol purification was carried out under vacuum and with a column of five theoretical stages and a reflux ratio of 2.

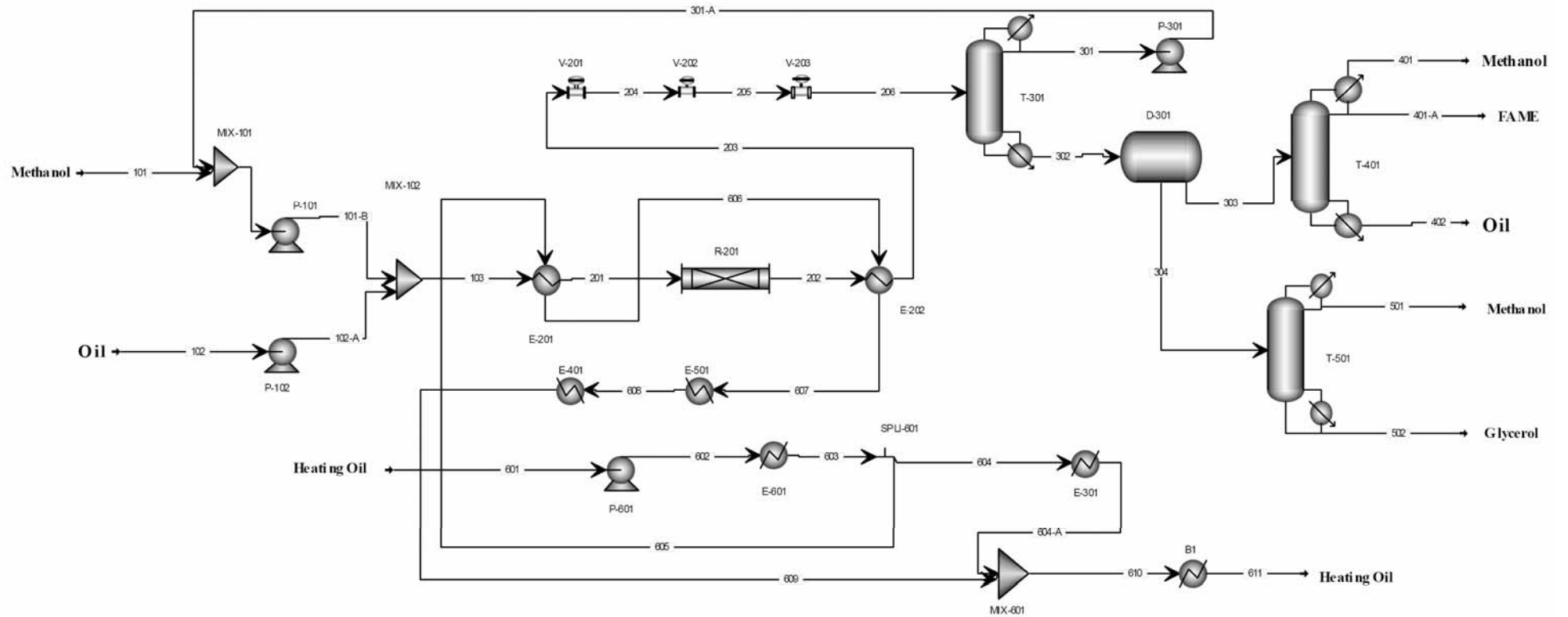


Figure 1. The process flowsheet

3. RESULTS

The product characteristic and energy consumption for all simulations performed in this study is shown in **Table 2**. As can be seen the energy consumption depends mainly on degree of conversion of triglycerides and on used methanol:oil ratio in synthesis. The lowest value of energy necessary for production 1 kg of FAME being in the case of synthesis at subcritical condition (simulation V) with smallest ratio of methanol:oil (15:1). Comparing simulation II and III, one can conclude that for the same degree of conversion and for large difference in reaction temperature and pressure the total energy consumption is almost the same (difference is almost negligible). The energy which might be obtained from the reaction mixture leaving reactor could be used in corresponding heat exchangers system. That means that synthesis realized under supercritical condition i.e. at high temperature and also under high pressure don't have significant influence on total energy consumption for supercritical biodiesel production.

Table 2. Product characteristic and energy consumption for a production of 10,000 tones/year

	Simulation I	Simulation II	Simulation III	Simulation IV	Simulation V
Product characteristic					
FAME purity, mass%	99.8	99.8	99.8	99.4	99.8
(yield, kg/h)	1136,9	1226.7	1226.7	1283.08	1226.8
Other component in FAME* mass%					
-Trioleine	0.000009	0.186	0.186	0	0.151
-Glycerol	0.062	0.00453	0.00453	0.052	0.0135
-Methanol	0.178	0.009	0.009	0.548	0.0795
Glycerol purity, mass%	96.4	96.4	96.4	95.5	96.4
(yield, kg/h)	125.4	135.3	135.3	137.6	135.2
Energy consumption, kW					
Equipment					
Reactor	-4.67	-11.38	-4.64	-11.46	-4.62
Preheater	414.17	1157.80	345.42	1114.34	180.37
Pumps	30.67	35.87	25.58	43.53	15.15
Recovery of methanol (reboiler)	1778.50	1503.86	1504.39	1467.95	430.06
Purification of FAME (reboiler)	886.01	530.87	530.87	-	560.75
Purification of glycerol (reboiler)	25.26	8.56	8.56	3.47	8.56
Heat exchanger	-	-815.39	-	-790.67	-
Total	3,134.61	2,421.57	2,414.82	1,838.62	1,194.89

However, results of these simulations indicate that degree of conversion has a significant influence on the energy necessary for purification of methyl esters and glycerol. For theoretical conversion of 100% (IV simulation) the purification of FAME step is not necessary but if degree of

conversion is increased from 80.9 to 97 % (simulation I and II) the energy consumption necessary for purification step decreases for 40%.

The main energy consumed phase in supercritical (or subcritical) methanolysis is recovery of excess of methanol from reaction mixture. Comparing the simulation II and V (the same reaction pressure and temperature and the same degree of conversion; **Table 2**) obviously that decrease of methanol to oil ratio from 42:1 to 15:1 substantially reduces total energy consumption for 50%. Such change of process condition has also influence on the energy necessary for preheating reaction mixture as well as for pumping it to desired pressure.

4. Conclusion

Several simulations of FAME synthesis under high temperature and pressure (subcritical and supercritical condition; non-catalyzed synthesis and heterogeneous process) assuming fixed production of biodiesel 10,000 tones and 7,900 working hours per year were analyzed by ASPEN Plus® v2006 software. Results of these simulations, based on assumption that simple irreversible reaction rate of the first-order is valid, indicated that the highest energy consumption per 1 kg of produced FAME is in the case of non-catalytic synthesis at subcritical condition, and that energy consumption depends mainly on degree of conversion of triglycerides. Thus, the value of energy consumption for supercritical methanolysis could be almost 25% smaller if degree of conversion could be increased from 97 mass% to 100 mass% (II vs. IV simulation). Substantial decrease of energy consumption could be obtained at subcritical condition only if methanol:oil ratio can be drastically changed (from 42:1 to 15:1). Realization of FAME synthesis at working conditions (P, T and methanol:oil ratio) proposed in simulation V requires use of heterogeneous catalyst³. This study and obtained results of several simulations obviously indicated that future economy of FAME synthesis mainly depends on development of efficient heterogeneous catalyst.

5. References

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Acknowledgements

The financial support of the Ministry of Science and Environmental Protection of the Republic of Serbia project No ON 142073 is gratefully acknowledged.