

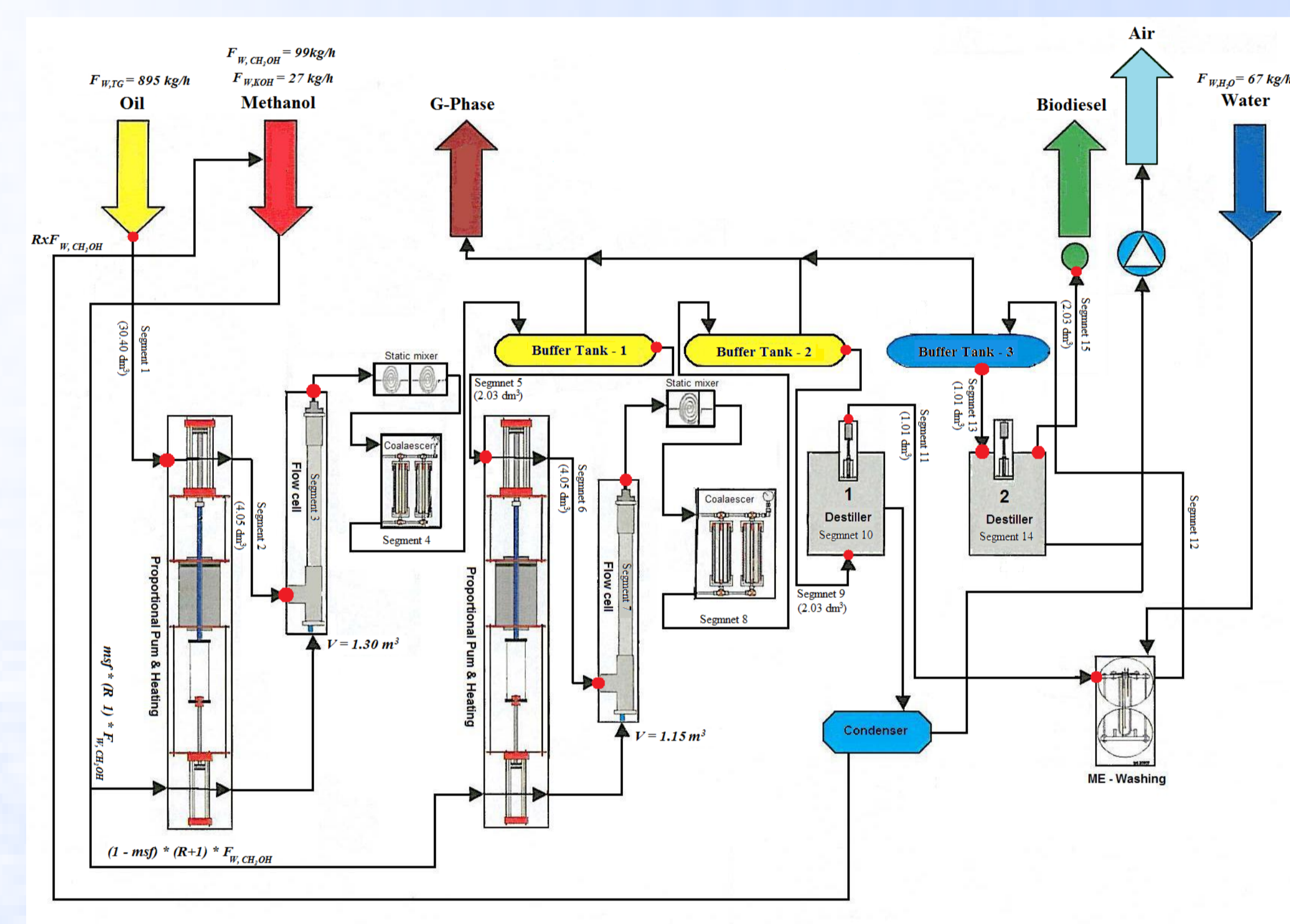
Introduction

In this study the transesterification of rapeseed and waste sunflower oils with methanol in the presence of potassium hydroxide as a catalyst was investigated. The transesterification of the investigated tri-acylglycerols was conducted in a batch reactor. The effect of the temperature (40 °C and 50 °C) on the rates of the reactions was studied at a constant molar ratio of alcohol to tri-acylglycerols (6:1) and at a constant concentration of the catalyst (1.0 wt %). Size exclusion chromatography (SEC) was used to quantitatively monitor the transesterification reaction of rapeseed and waste sunflower oils to mono-alkyl esters. The results were correlated with the results obtained by ¹H NMR spectroscopy. Three stepwise and reversible reactions were assumed to occur. Mass transfer limitations were considered for various temperatures. The reaction rate constants for the transesterification of tri-, di- and mono-acylglycerols were determined based on a mathematical model, describing the kinetics of transesterification. The activation energies of particular reactions were evaluated from the reaction rate constants, determined at two temperatures. The parameters extracted from the laboratory data were applied for an industrial setup.

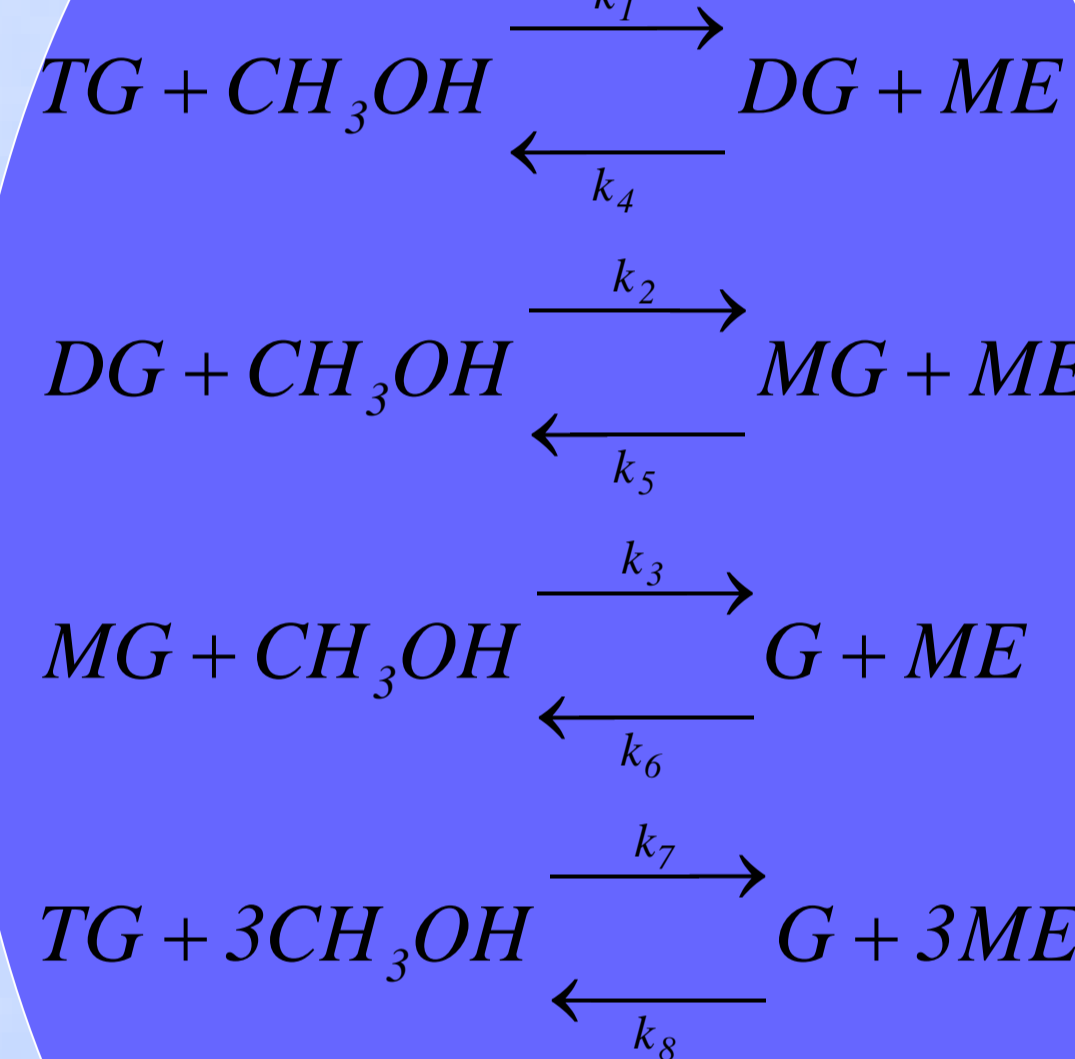
Experimental

The transesterification reaction was performed in a 1 L three-necked flask equipped with a sampling port, a thermometer and a mechanical stirrer. The mechanical stirrer assures a constant mixing intensity with a rotational speed of 500 rpm. The reactor flask, filled with 500 g of oil, was heated to the desired temperature. Then a measured amount of the potassium hydroxide in methanol solution, which was heated separately, was added and the mechanical stirrer was started. The reaction was timed as soon as the mechanical stirrer was turned on. A 6:1 molar ratio of methanol to oil was used.

Based on the data obtained from the experimental work on the laboratory scale and the subsequent modeling, operations in a continuous industrial setup were predicted. The data was taken from the first reactor outflow and at the overall industrial setup BDT CPU1000 outflow (Scheme 1). The system was operating at different process temperatures (depending on unit operation) with corresponding variable residence times. Continuous industrial-scale multi-stage alkaline transesterification was initiated with methanoate (methanol with dissolved KOH catalyst) and rapeseed oil being heated to principal reactions' process temperature (58 °C).



Scheme 1: The scheme of continuous reactor/separators setup BDT CPU1000.



Results

Size exclusion chromatography (SEC) and ¹H NMR spectrometry

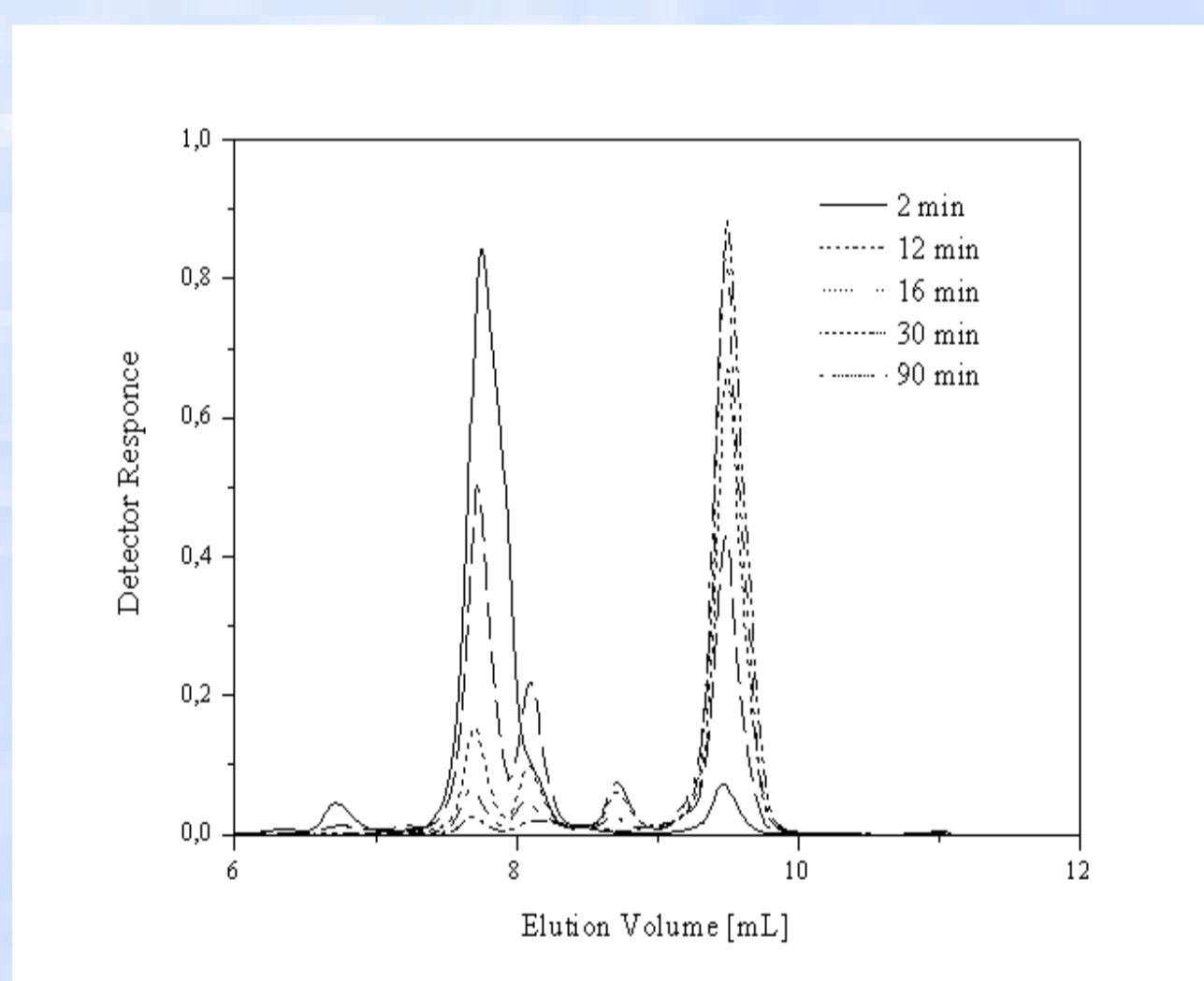


Fig. 1: SEC chromatograms of TG consumption for transesterification of waste sunflower oil at 40 °C.

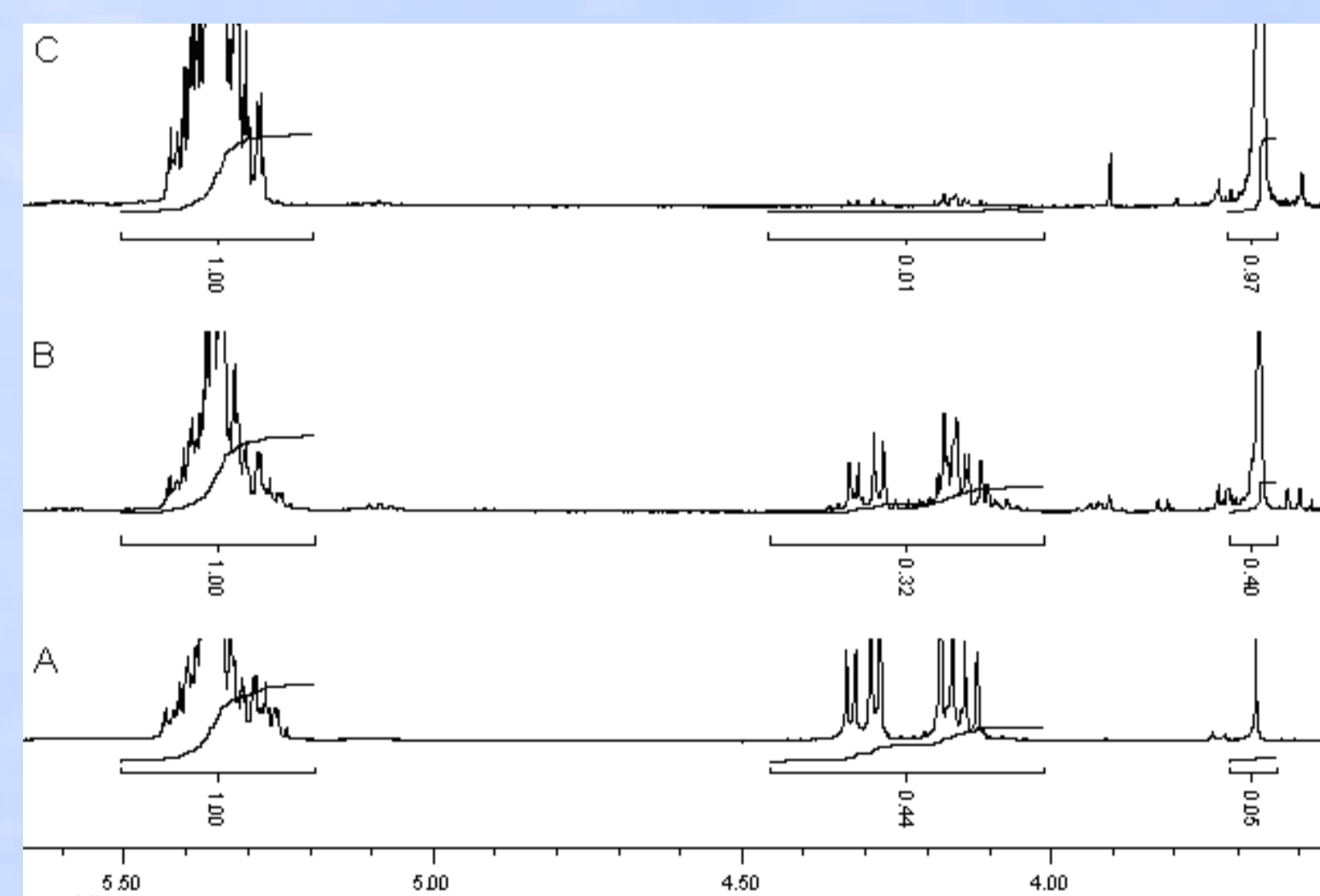


Fig. 2: ¹H NMR spectra of the transesterification in progress, where A, B, and C denotes 2, 12, and 90 min of the reactions' time, respectively.

$$[ME] = \frac{4 \times I_{ME}}{4 \times I_{ME} + 9 \times I_{TG}}$$

I_{ME} is the integration value of the methyl ester peak and
 I_{TG} is the integration value of the acylglycerol peaks in the tri-acylglycerols of vegetables oils

Table 1: Activation energies of reactions for waste sunflower oil (SO) and rapeseed oil (RO) methanolysis with 1 wt. % of KOH catalyst (per oil weight), methanol to oil molar ratio of 6:1, and modeling with (s. r.) and without (no s. r.) shunt reaction.

Activation energy (kJ/mol)	SO no s. r.	SO s. r.	RO no s. r.	RO s. r.
$E_{A,1}$	95.9	92.5	57.6	35.9
$E_{A,2}$	92.8	105.7	60.3	19.2
$E_{A,3}$	27.3	35.5	74.0	47.2
$E_{A,4}$	241.3	248.4	58.2	76.9
$E_{A,5}$	48.1	189.6	86.3	51.6
$E_{A,6}$	63.5	165.4	21.3	35.6
$E_{A,7}$	–	66.9	–	116.6
$E_{A,8}$	–	230.5	–	24.2

Table 2: Reaction rate constants for waste sunflower oil (SO) and rapeseed oil (RO) methanolysis at temperatures 40 °C and 50 °C, with 1 wt. % of KOH catalyst (per oil weight), methanol to oil molar ratio of 6:1, and modeling with (s. r.) and without (no s. r.) shunt reaction.

Rate constant (l mol ⁻¹ min ⁻¹)	SO 40 °C	SO 40 °C	SO 50 °C	SO 50 °C	RO 40 °C	RO 40 °C	RO 50 °C	RO 50 °C
k_1	0.0247	0.0225	0.0772	0.0727	0.0443	0.0222	0.0879	0.0340
k_2	0.0558	0.0447	0.1680	0.1569	0.2334	0.1167	0.4777	0.1466
k_3	0.0703	0.0627	0.0972	0.0956	0.0645	0.0323	0.1555	0.0565
k_4	0.0015	0.0011	0.0265	0.0213	0.0699	0.0350	0.1396	0.0872
k_5	0.0394	0.0067	0.0670	0.0638	0.2681	0.1340	0.7478	0.2474
k_6	0.0042	0.0012	0.0088	0.0083	0.0047	0.0024	0.0061	0.0036
k_7	–	1.2×10^{-4}	–	2.6×10^{-4}	–	8.4×10^{-4}	–	3.4×10^{-3}
k_8	–	1.4×10^{-7}	–	2.2×10^{-6}	–	1.4×10^{-5}	–	1.8×10^{-5}

Mass transfer limited heterogeneous regime

Taking into account that the mass transfer limited heterogeneous regime accounts in the extreme case (40 °C) for only 0.4 % of the total reaction time (100 min), it is justified to surmise that the prevailing regime is the pseudo-homogenous kinetics limited one.

Table 3: The duration of the mass transfer controlled regime (t_{MT}) and the TG mass transfer coefficient (K_L) at different reaction temperatures for waste sunflower oil (SO) and rapeseed oil (RO) using SEC and NMR data

T (°C)	t_{MT} (s)	$K_L \times 10^5$ (m/min)		
		(SO)	(RO)	(SO and RO)
40	7.4–26.6	0.20–0.28	0.35–0.48	4.42–4.98
50	1.7–7.9	0.88–1.16	0.40–1.02	11.36–13.15
58	0.5–3.0	–	–	–

Kinetics limited pseudo-homogenous regime in laboratory batch reactor

$$\frac{\partial [TG]}{\partial t} = -k_1 \times [TG] \times [CH_3OH] + k_4 \times [DG] \times [ME] - k_7 \times [TG] \times [CH_3OH]^3 + k_8 \times [G] \times [ME]^3$$

$$\frac{\partial [DG]}{\partial t} = k_1 \times [TG] \times [CH_3OH] - k_2 \times [DG] \times [CH_3OH] - k_4 \times [DG] \times [ME] + k_5 \times [MG] \times [ME]$$

$$\frac{\partial [MG]}{\partial t} = k_2 \times [DG] \times [CH_3OH] - k_3 \times [MG] \times [CH_3OH] - k_5 \times [MG] \times [ME] + k_6 \times [G] \times [ME]$$

$$\frac{\partial [G]}{\partial t} = k_3 \times [MG] \times [CH_3OH] - k_6 \times [G] \times [ME] + k_7 \times [TG] \times [CH_3OH]^3 - k_8 \times [G] \times [ME]^3$$

$$\frac{\partial [CH_3OH]}{\partial t} = -k_1 \times [TG] \times [CH_3OH] - k_2 \times [DG] \times [CH_3OH] - k_3 \times [MG] \times [CH_3OH] + k_4 \times [DG] \times [ME] + k_5 \times [MG] \times [ME] + k_6 \times [G] \times [ME] - 3 \times k_7 \times [TG] \times [CH_3OH]^3 + 3 \times k_8 \times [G] \times [ME]^3$$

$$\frac{\partial [ME]}{\partial t} = k_1 \times [TG] \times [CH_3OH] + k_2 \times [DG] \times [CH_3OH] + k_3 \times [MG] \times [CH_3OH] - k_4 \times [DG] \times [ME] - k_5 \times [MG] \times [ME] - k_6 \times [G] \times [ME] + 3 \times k_7 \times [TG] \times [CH_3OH]^3 - 3 \times k_8 \times [G] \times [ME]^3$$

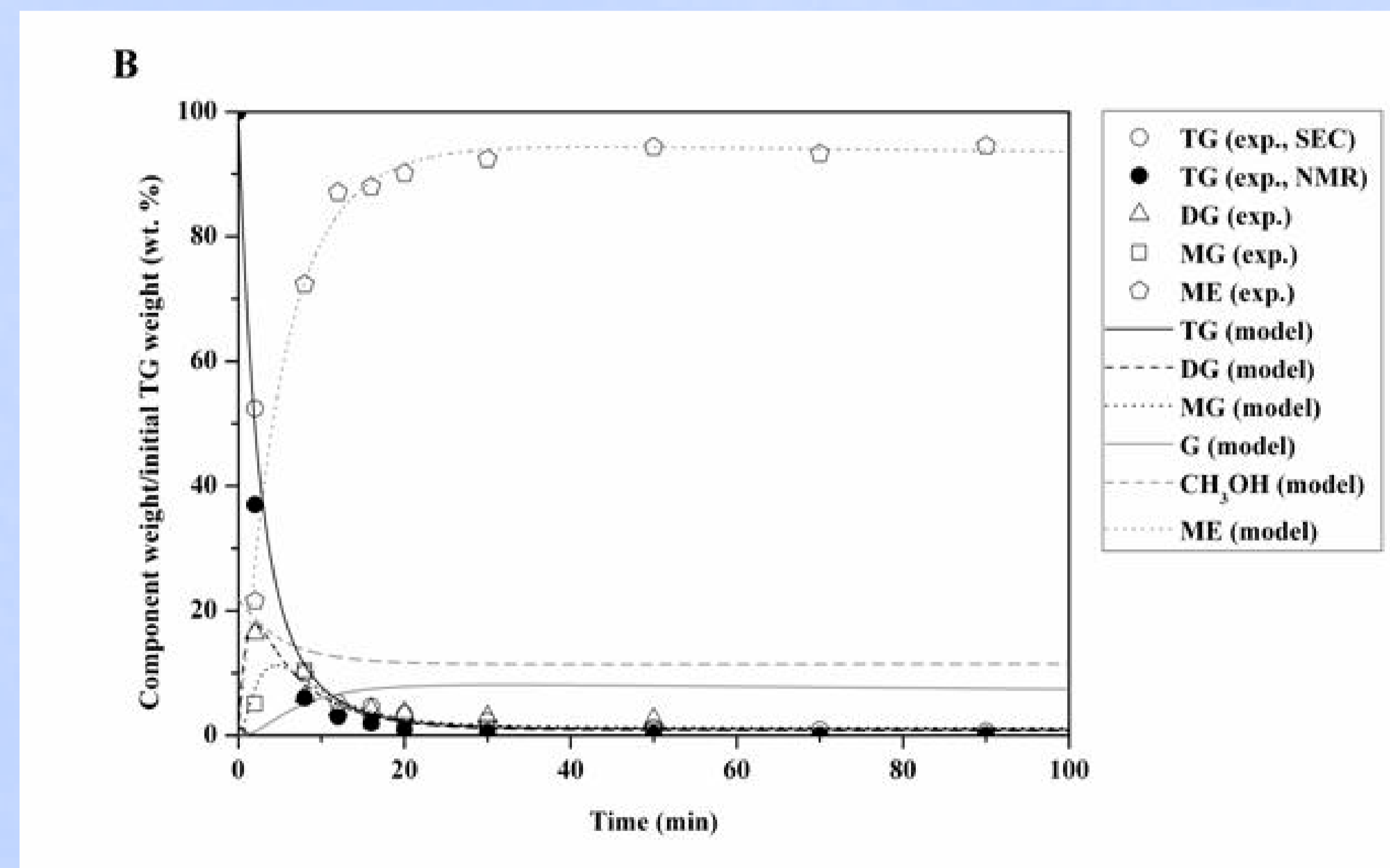


Fig. 3: Experimental results and kinetics model predictions for the product distribution for transesterification of waste sunflower oil at 50 °C.

Kinetics limited pseudo-homogenous regime in industrial plug flow reactor series



Fig. 4. Experimental points and simulation curves for the component concentrations in the mixture during the transesterification reactions/separations in the industrial setup with varying catalyst concentration and different residence times at specific unit operations.

Conclusions

Fatty acid methyl esters demonstrate great potential when applied as a diesel substitutes and they are known as a biodiesel. The obtained reaction rate constants show that the transesterification of rapeseed and waste sunflower oil is sensitive to temperature and that the transesterification of waste sunflower oil proceeds faster than the natural rapeseed oil. The results examining both mass transfer and kinetics suggest that in the temperature range studied, the rates of the forward reactions of the transesterification dominate. Data from the laboratory experiments was used to successfully predict the operations on the industrial scale.

References

- Darnoko, D., Cheryan, M., 2000. Kinetics of palm oil transesterification in a batch reactor. *J. Am. Oil Chem. Soc.* 77 (12), 1263–1267.
- Freedman, B., Butterfield, R. O., Pryde, E. H., 1986. Transesterification Kinetics of Soybean Oil. *J. Am. Oil Chem. Soc.* 63, 1375–1380.
- He, H. Y., Sun, S. Y., Wang, T., Zhu, S. L., 2007. Transesterification Kinetics of soybean oil for production of biodiesel in supercritical methanol. *J. Am. Oil Chem. Soc.* 84 (4), 399–404.
- Karim, S. K., Chandna, D., Ravi, R., Chadha, A., 2006. Kinetics of base-catalyzed transesterification of triglycerides from Pongamia oil. *J. Am. Oil Chem. Soc.* 83 (10), 873–877.
- Knothe G., 2000. Monitoring a Progressing Transesterification Reaction by Fiber-Optic Near Infrared Spectroscopy with Correlation to ¹H Nuclear Magnetic Resonance Spectroscopy. *J. Am. Oil Chem. Soc.* 77, 489–493.
- Nooredini, H., Zhu, D., 1997. Kinetics of transesterification of soybean oil. *J. Am. Oil Chem. Soc.* 74 (11), 1457–1463.
- Stamenkovic, O. S., Todorovic, Z. B., Lazić, M. L., Veljkovic, V. B., Skala, D. U., 2008. Kinetics of sunflower oil methanolysis at low temperatures. *Biore. Technol.* 99 (5), 1131–1140.