CHAPTER IV

EFFECT OF CO-SOLVENTS

4.1. Reaction among vegetable oil, methanol and co-solvents

To ensure that the reaction between co-solvent and other reactants did not occur, the GC-MS chromatograms of mixed methyl esters standard and biodiesel products, obtained from employed THF at 350 °C and the methanol to oil molar ratio of 42:1 and THF of 5 mol in vegetable oil at reaction time of 10 min, were obtained as illustrated in Figures 4.1 and 4.2.

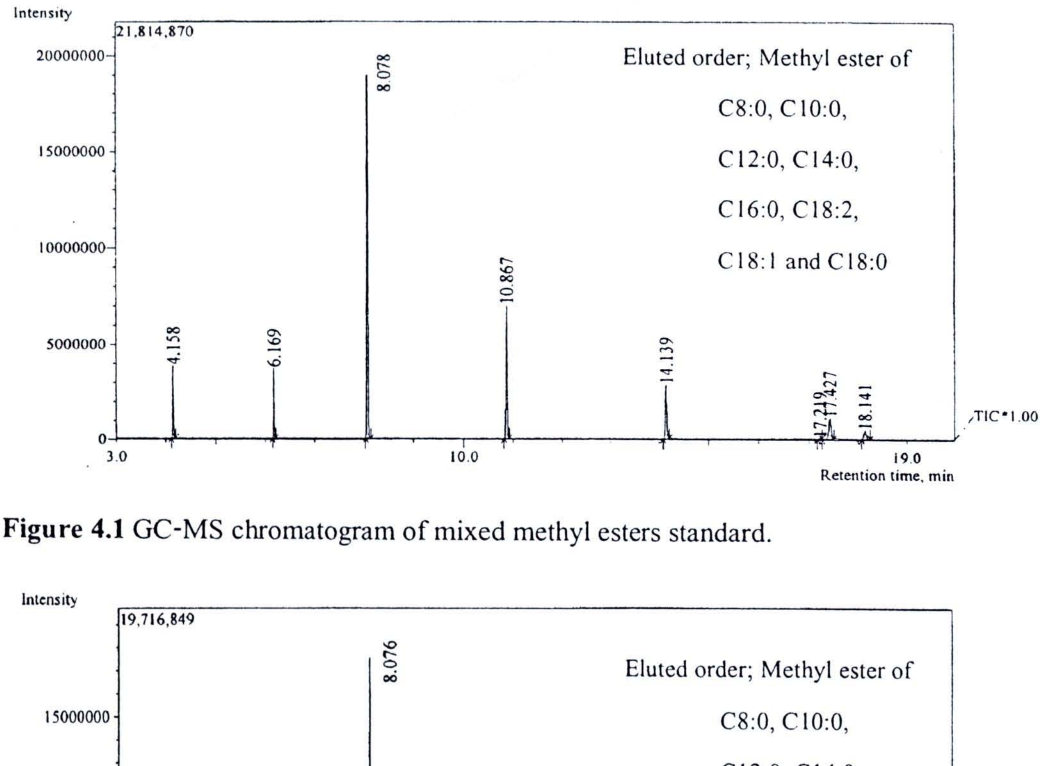

Figure 4.1 GC-MS chromatogram of mixed methyl esters standard.

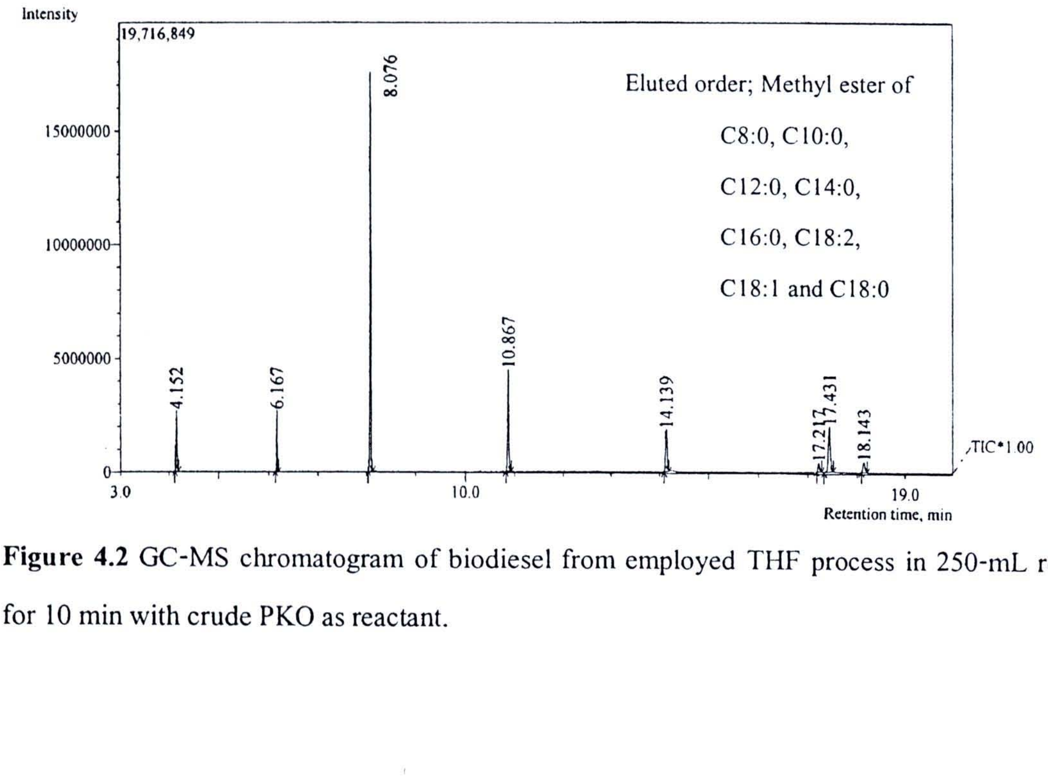

Figure 4.2 GC-MS chromatogram of biodiesel from employed THF process in 250-mL reactor for 10 min with crude PKO as reactant.

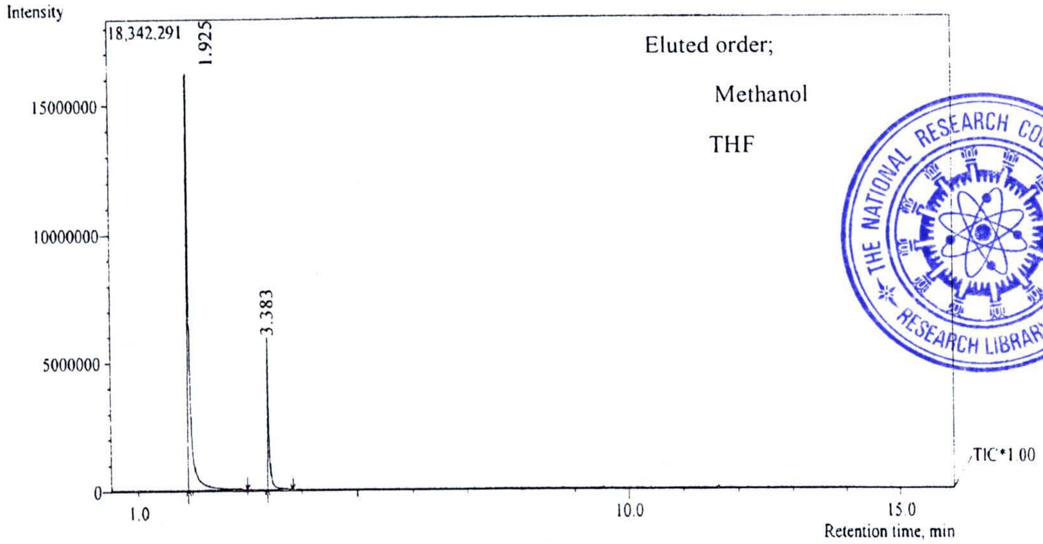

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Figure 4.3 GC-MS chromatogram of THF phase in 250-mL reactor for 10 min with crude PKO as reactant.

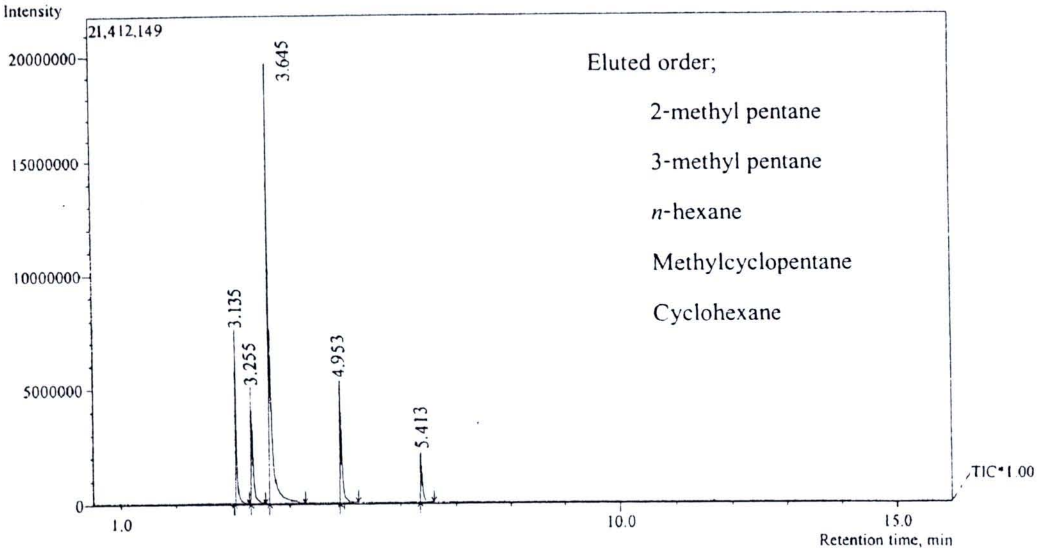

Figure 4.4 GC-MS chromatogram of hexane phase in 250-mL reactor for 10 min with crude PKO as reactant.

Comparing Figure 4.1 with Figure 4.2, it can be seen that the biodiesel composition from the employed THF process was basically the same as the mixed fatty acid methyl esters standard. On the other hand, from the THF and hexane chromatograms in Figures 4.3 and 4.4, one can deduce that THF and hexane peaks did not show up in Figure 4.2. Therefore, it is concluded that there was no co-solvent interference in the transesterification reaction.

4.2. Effect of co-solvents on ME content in a 250-mL reactor

The experimental order (Table 4.1 and run order 1 to 12 in Table 4.2) was done randomly. For run order 13 to 20 in Table 4.2, i.e. the co-solvent free process, the experimental data were obtained from Table 4.1.

To eliminate the effect of pressure, the amount of reactants and co-solvent was adjusted to a specified pressure (19.0 MPa) by using the Redlich-Kwong Equation of State and the Lorentz-Berthelot-type mixing rule [86]. Unfortunately, the calculated pressure was not exactly equal to the observed pressure. In some experiments, where there was a large difference between the calculated and observed pressure, the amounts of reactant and co-solvent were readjusted by trial and error. The observed pressures for each experiment are shown in Tables 4.1 and 4.2.

All experimental data were analyzed by the factorial design procedure [87] to obtain the analysis of variance tables (ANOVA), which are shown in Tables 4.3 and 4.4.

Table 4.1 Experimental data from employed THF process in 250-mL reactor for 10 min with crude PKO as reactant

Run order	Temperature (°C)	Pressure (MPa)	THF to oil molar ratio	MeOH to oil molar ratio	ME content (%wt)
1	350	17.9	0.0	12.1	79.7
2	290	17.5	5.6	41.3	72.6
3	350	19.3	4.8	39.9	86.5
4	290	17.4	5.0	41.9	73.2
5	350	19.0	0.0	41.3	84.9
6	290	16.6	0.0	42.2	63.7
7	320	19.0	2.4	24.0	79.6
8	350	19.8	5.0	12.2	79.6
9	320	17.8	2.5	23.9	80.4
10	350	19.4	4.9	41.9	79.3
11	350	19.8	0.0	12.1	80.9
12	320	19.1	2.6	24.1	79.7
13	350	19.6	0.0	42.1	85.1
14	290	16.3	5.1	11.9	45.0
15	350	21.6	5.1	12.1	82.5
16	290	15.6	0.0	12.1	43.7
17	290	16.2	0.0	11.2	47.6
18	290	15.9	5.1	12.3	47.3
19	320	18.0	2.5	24.1	78.6
20	290	16.9	0.0	42.1	62.3

Table 4.2 Experimental data from employed hexane process in 250-mL reactor for 10 min with crude PKO as reactant

Run order	Temperature (°C)	Pressure (MPa)	Hexane to oil molar ratio	MeOH to oil molar ratio	ME content (%wt)
1	290	19.6	4.7	41.3	62.4
2	350	18.7	4.6	40.9	87.6
3	290	19.2	5.1	12.4	46.2
4	290	20.0	4.8	42.6	65.2
5	350	18.6	5.0	12.4	79.8
6	320	19.2	2.5	24.2	77.8
7	290	20.0	4.9	12.2	48.5
8	320	18.6	2.6	24.3	78.2
9	350	17.7	5.0	43.4	88.1
10	320	18.2	2.5	24.2	76.5
11	320	19.6	2.4	24.1	76.6
12	350	19.0	5.2	12.4	85.9
13	290	15.6	0.0	12.1	43.7
14	290	16.2	0.0	11.1	47.6
15	350	19.8	0.0	12.1	80.9
16	350	17.9	0.0	12.1	79.7
17	290	16.6	0.0	42.2	63.7
18	290	16.9	0.0	42.1	62.3
19	350	19.6	0.0	42.1	85.1
20	350	19.0	0.0	41.3	84.9

Table 4.3 Analysis of variance from employed THF process in 250-mL reactor for 10 min with crude PKO as reactant

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob. > F
A (Temperature)	2583.77	1	2583.77	69.47	< 0.0001
B (THF to oil)	18.28	1	18.28	0.49	0.4966
C (MeOH to oil)	538.21	1	538.21	14.47	0.0025
AB	31.45	1	31.45	0.85	0.3759
AC	338.75	1	338.75	9.11	0.0107
BC	10.41	1	10.41	0.28	0.6065
ABC	39.51	1	39.51	1.06	0.323
Residual	446.29	12	37.19		
Total	4043.78	19			

Table 4.4 Analysis of variance from employed hexane process in 250-mL reactor for 10 min with crude PKO as reactant

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob. > F
A (Temperature)	3374.01	1	3374.01	142.32	< 0.0001
B (Hexane to oil)	15.18	1	15.18	0.64	0.4391
C (MeOH to oil)	421.18	1	421.18	17.77	0.0012
AB	2.16	1	2.16	0.091	0.7679
AC	141.41	1	141.41	5.96	0.0310
BC	4.314E-03	1	4.32E-03	1.8E-04	0.9895
ABC	0.082	1	0.082	3.4E-03	0.9539
Residual	284.49	12	23.71		
Total	4249.48	19			

From Tables 4.3 and 4.4, the molar ratio of co-solvent to oil (factor B) and its interaction (factors AB, BC and ABC) had no significant effect on ME content, as noticed from the probability of F value less than 0.05, at the confidence level of 95%. Thus, it was concluded that the addition of a co-solvent in this process did not show either negative or positive effect on ME content.

The regression models in terms of coded units of employed THF and hexane process can be then correlated as shown in Equations 4.1 and 4.2, respectively.

$$\%ME = 71.88 + 12.67A + 5.90C - 4.67AC \qquad (4.1)$$

$$\%ME = 71.21 + 14.53A + 5.12C - 2.99AC \qquad (4.2)$$

where *%ME* is ME content in biodiesel product (%wt)

A is temperature in terms of coded unit, derived by the Equation (4.3)

$$A = \frac{\text{Temperatur e } (^\circ\text{C}) - 320}{30} \qquad (4.3)$$

C is the methanol to oil molar ratio in terms of coded unit, derived by the Equation (4.4)

$$C = \frac{\text{Mole of MeOH (mole)} - 27}{15} \qquad (4.4)$$

Temperature (A) and the methanol to vegetable oil molar ratio (C) has positive effects on ME content, and the temperature effect has a higher magnitude than the methanol to oil molar ratio effect by approximately two folds. It should be noticed that temperature and methanol to oil molar ratio had an interaction due to the amount of methanol affect the transition temperature as mentioned in section 2.4.3. The interaction term (AC) indicated the complete regression model might be of second order; which is consistent with our previous finding [20].