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# Potential Utilization of Fusel Oil: A Kinetic Approach for Production of Fusel Oil Esters Through Chemical Reaction

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Fusel oil is a by-product of the distillation of ethyl alcohol from the fermentation of molasses and contains mainly C3-C5 alcohols. Acetic acid and butyric acid esters of its major alcohol components have economic value as chemicals for flavor and fragrance manufacturing. This study presents some data regarding the uncatalyzed esterification of fusel oil with acetic acid, propionic acid and butyric acid. The reactions were carried out at two temperatures, i.e., 45° C and under the reflux conditions (80 – 85° C). The composition of raw fusel oil and the reaction mixtures were determined by gas chromatography. The reaction rate constants for the formation the esters were estimated based on the concentration-time relationships. The results indicated that esterification rate of fusel oil is very slow and, under identical conditions, the rate depends on the reacting acid. The formation rates of butyric acid esters were found to be higher than the those of acetic acid and propionic acid esters. After approximately 6.5 hours of the reaction at 45° C, the estimated maximum production yield of the mixed acedic acid esters was around 19%, propionic acid esters 24% and butyric acid esters 35%. Increasing reaction temperature increased the conversion ratios.

**Keywords:** fusel oil, esterification, kinetics)

## Introduction

One of the main products of sugar manufacturing is molasses, which contains approximately 50% sucrose and 50% other components (water, various other organic components and inorganic salts).<sup>1,2</sup> Because of its high sucrose content, a substantial portion of the molasses is used for the production of ethyl alcohol through fermentation. In recent decades, 12 million tons of sugar beet have been processed and approximately 550 thousand tons of molasses have been obtained per year, in Turkey.<sup>3</sup> Approximately, 30 million liters of ethyl alcohol per year is produced from these molasses. The by-products of the fermentation broths, more volatile than the alcohol, are mainly aldehydes with acetaldehyde being the principal component.<sup>4</sup> The aldehyde is removed, as a distillation head product. The other by-product of the distillation step, the bottom product, is fusel oil. It is composed of several alcohols, primarily C3, C4 and C5 aliphatic alcohols. Approximately 1 l of acetaldehyde and 5 l of fusel oil are obtained for every 1000 l of ethyl alcohol from the distillation.<sup>4</sup> Raw fusel oil is a relatively viscous liquid with a dark-reddish color and a very unpleasant odor. As a

result of these properties, the direct utilization of fusel oil as a solvent has been very limited. In some countries it is burned to supply energy for processing plants.<sup>5</sup> In Turkey, it is used mainly for denaturation of alcohol or for removing the foam from molasses during sugar manufacturing. A substantial portion of it, however, has generally been discarded.<sup>3</sup> Recent studies have suggested that several alternatives uses for fusel oil are possible. For example, acetic acid and butyric acid esters, major alcohol components of fusel oil, have economic value as chemicals for flavor and fragrance manufacturing. Especially ethylbutyrate is in high demand as a component of pineapple-banana flavors in the food industry.<sup>5-7</sup> Seino et.al.<sup>8</sup> investigated the enzymatic synthesis of the carbohydrate esters of fatty acids. Gilles, et.al.<sup>6</sup> and Welsh and Williams<sup>5</sup>, studied enzymatic esterification of fusel oil with acetic acid and butyric acid. Generally lipase enzyme was used in these studies. Ghuiba et.al.<sup>9</sup> investigated chemical esterification of fusel oil with polybasic acids with high molecular weights at relatively high temperatures. They reported that the esters synthesized under these conditions are very compatible with polyvinyl chloride as plasticizers. Ay et.al.<sup>10</sup> reported that fusel oil can be used for the purification of phosphoric acid produced by the wet method. They also reported that especially iso-amyl alcohol and iso-butyl alcohol are effective for the extraction of the acid. Hasan et.al.<sup>11</sup> reported that the indigenously prepared solvent triisoamyl phosphate (TAP) obtained from fusel oil has been successfully utilized to extract titanium (IV) from its aqueous solutions. Various other studies have also indicated that fusel oil has potential as a valuable raw chemical.<sup>12-14</sup>

Various data on the lipase mediated esterification of fusel oil are given in the literature. However, data on its chemical esterification with low molecular weight monobasic organic acids are very limited. Therefore, it seemed appropriate to investigate the chemical esterification. This paper reports some preliminary results for the formation of various esters from fusel oil. The distilled fusel oil was reacted with acetic acid, propionic acid and butyric acid. The formation of the esters was traced by gas chromatography (g.c.). In order to get further information about the reaction rates, the time-concentration relations were investigated in terms of classical reaction kinetics. No attempt was made at this stage to separate or purify the products.

## Experimental

### *Sample Preparation*

A fusel oil sample was supplied by the Malatya Sugar Factory. A definite amount of raw fusel oil (10 ml) was shaken with various amounts of water-saturated hexane. Maximum phase separation was observed at a volume ratio of approximately 1:1. The water content of the fusel oil was determined by measuring the amount of water after phase separation. Following the removal of water phase, Na<sub>2</sub>SO<sub>4</sub> was added (approximately 0.15 g of the salt per cubic centimeter of fusel oil) to reduce the water content of the fusel oil. The raw or dried fusel oils were subjected to simple distillation by using a fraction head with a height of 50cm. The fusel oil was separated into weight fractions with different boiling ranges by collecting the distillates at various temperature intervals. Based on amounts of distillates and average distillation temperature, the evaporation curves for both raw and dried fusel oil were determined.

### *Esterification of Fusel Oil*

The distilled and dried fusel oil was reacted with organic acids (glacial acetic acid, propionic acid or butyric acid) at two temperatures, i.e., 45° C ( $\pm 2^\circ$  C) or under reflux conditions (80 – 85° C). A constant stirring rate of approximately 100 rpm was used during the reaction. The reaction mixtures were prepared by mixing approximately equimolar amounts of the acids and fusel oil. In a typical experiment, 120 g of fusel oil, (approximately 1.563 mol) was reacted with 90 g of glacial acetic acid (1.493 mol). Similar ratios were used in the other reactions. In some reactions, an equal volume of hexane was added to the above mixture

(total volume about 380-400 ml) to bring about the reaction under nonaqueous conditions. Samples were withdrawn from the mixtures during the reaction approximately every half hour.

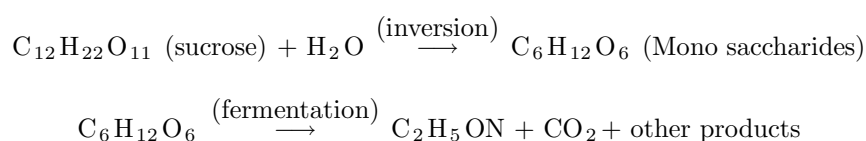
#### *G.c. Analysis*

The composition of the raw fusel oil, the distillate fractions and that of the reaction mixtures were determined by g.c. A Unicam 6100 series gas chromatograph interfaced with a data system and equipped with FID and TCD was used in the analyses. A J&W Scientific fused silica capillary column (15 m × 0.249 mm i.d., coated with DB-1 in a film thickness of 0.25 μm) was used in the analyses. The temperature was 50°C for 2 min. and 50 – 130°C at 4°C/min. The injector temperature was 160°C and the detector temperature was 220°C. Nitrogen was used as the carrier gas and a split ratio of 1:50 was applied during the analyses. The flow rate for the carrier gas was 2 ml/min and for the make-up gas 30 ml/min. The detector gases were 30 ml/min. and 300 ml/min. for hydrogen and air, respectively.

Two different standard solutions with known quantitative compositions were prepared for the analysis of each type of sample i.e., for fusel oil and the reaction mixtures. C2-C5 alcohols, acetic acid, propionic acid and butyric acid were used in the preparation of the standard solutions. In addition, a series of binary mixtures were also prepared by mixing the pure alcohols and the pure acids. These binary mixtures were also analyzed under identical conditions after approximately 12 hours of the reaction at room temperature. 0.01 μl of the sample was injected each time and average analysis time was around 30 min. Identification and quantifications were carried out by comparing the chromatograms of samples with those of standard solutions. The peaks in the chromatograms of the samples were identified by matching the retention times with the peaks of pure components and the standard solutions. Relative FID response factors were determined by comparing the known compositions and the determined compositions of the standard solutions.

## Results and Discussions

Fermentation is a complex biological process and is generally promoted and catalyzed by microorganisms or enzymes. It is widely used to produce alcoholic beverages, antibiotics, foodstuffs, and to purify organic waste etc. An organic feed is converted to chemical products through fermentation. The main reactions which occur during the fermentation of molasses may be summarized as follows (5):



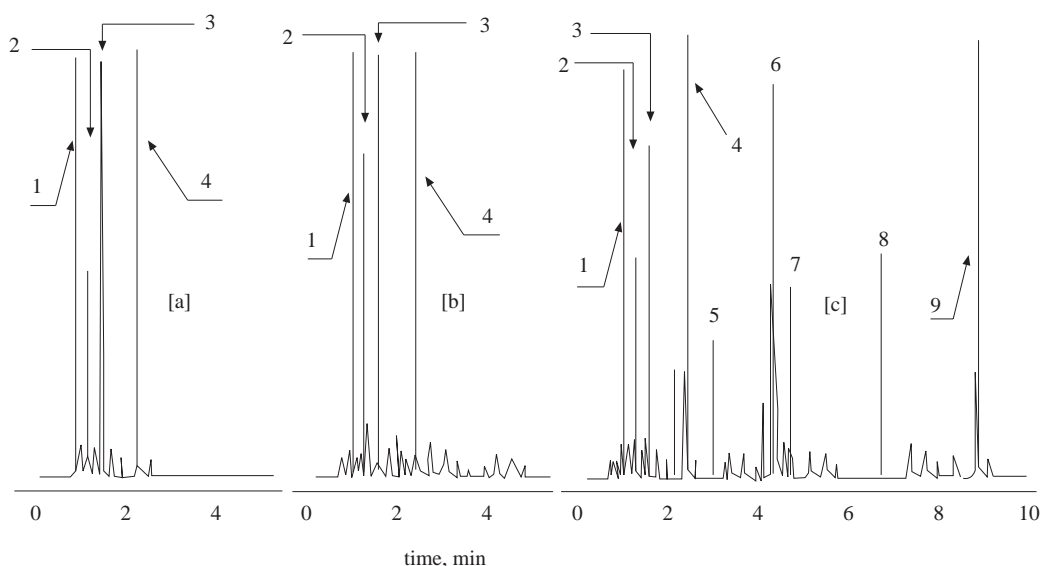
The reaction are, in fact, more complex and the fermentation broth contains many by-products. Sucrose, proteins and the other organic materials present in molasses undergo decomposition. Primary alcohols, aldehydes, acids and esters are produced during the fermentation. Therefore, fusel oil has a complex composition.

#### *G.c. Analysis of the Fusel Oil*

Fusel oil is generally analyzed by g.c. or h.p.l.c.<sup>6,15-17</sup> The studies in the literature indicate that fusel alcohols and their esters, and the other low boiling components can be simultaneously analyzed by a direct injection method g.c.. Generally, standard mixtures are used for both qualitative and quantitative analyses. FID was preferred in the g.c. because the response of FID is essentially independent of temperature, carrier gas and flow rate. This makes FID well suited, possibly the best detector for quantitative analysis. However, the detector responses are not same for all the compounds, i.e., the areas are not directly proportional to

the percent composition. Therefore, it is necessary to determine correction factors for a reliable quantitative analysis. The response factors given by Dietz<sup>18</sup> may be used in the quantitative analyses or can be determined by analyzing standard solutions with known compositions. A similar method was used in this study to determine the relative FID weight factors of the components. The raw g.c. data was modified using these factors.

The g.c. results showed that a good separation of the major components was achieved in the capillary column and a linear relationship exists between the peak area and compositions, in a wide range. Some representative chromatograms are given in Figure 1. In the quantitative analyses, both concentrated and sufficiently dilute solutions of the samples were used to test the linearity of detection. The results indicated that a dilution is not necessary in g.c. with a split ratio of 1:50. The results for the composition of the distilled fusel oil is given in Table 1. These results are averages of triplicate analyses, and the trace components (approximately up to 20 compounds) were ignored in the average composition. The repeated analyses showed that reproducibility of the method is very good and the relative deviation is around 5% or lower.



**Figure 1.** Some representative chromatograms: a: standard mixture, b: distilled fusel oil, c: reaction mixture of fusel oil and butyric acid after a reaction time of 60 minutes. Peak identifications: 1: ethyl alcohol, 2: n-propyl alcohol, 3: i-butyl alcohol, 4: i-amyl alcohol, 5: ethyl butyrate, 6: butyric acid, 7: propyl butyrate, 8: butyl butyrate, 9: i-amyl butyrate

**Table 1.** Average composition of the distilled fusel oil (wt. %, on water-free basis)

Component	wt %	mol %
ethyl alcohol	12.4	20.67
n-propyl alcohol	3.5	4.47
i-butyl alcohol	9.5	9.85
i-amyl alcohols	74.6	65.01

**Table 2.** Estimated rate constants for forward reactions (based on Eq. 5 or by extrapolation).

Time	$k_1 * 10^4$	$k_3 * 10^4$	$k_5 * 10^4$	$k_7 * 10^4$
acetic acid esterification				
30	2.796	3.264	3.839	4.735
65	2.523	2.945	3.464	4.272
96	2.089	2.437	2.864	3.527
00	3.10*	3.60*	4.20*	5.10*
propionic acid esterification				
30	3.483	3.942	4.777	5.446
65	3.171	3.589	4.349	5.138
95	2.614	2.957	5.578	4.221
00	3.80*	4.25*	5.20*	6.05*
butyric acid esterification				
39	2.837	3.217	3.875	5.923
96	2.791	3.167	3.822	5.239
151	2.490	2.824	3.402	4.647
00	3.25*	3.75*	4.50*	6.25*

$k_1, k_3, k_5, k_7$  are the apparent rate constants for esterification of ethyl alcohol, propyl alcohol, i-butyl alcohol, i-amyl alcohol, respectively.

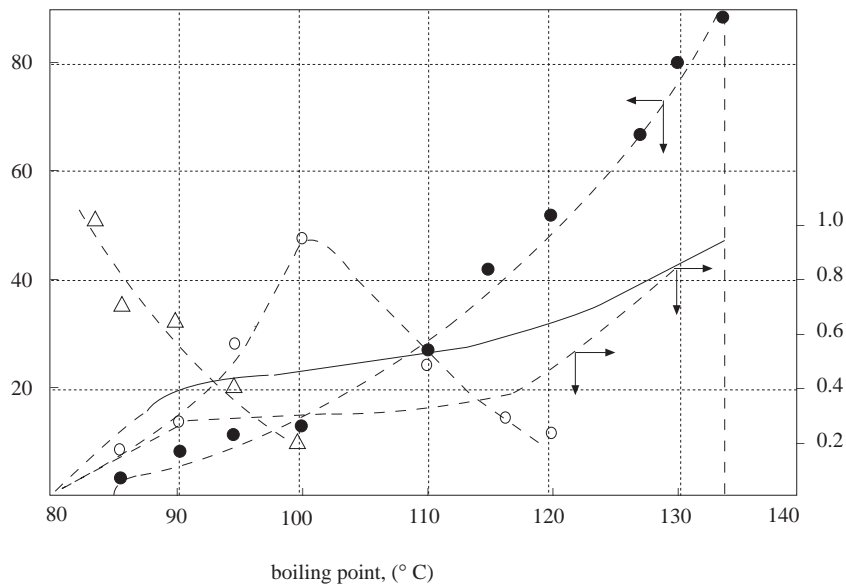
\*  $k_0$ , the rate constants estimated by extrapolation to zero reaction time for each reaction.

#### *Evaporation Curve of the Fusel Oil*

The water content of the fusel oil determined by the phase separation method was 14% on average. Recently Şaşmaz et.al.<sup>16</sup> reported that anhydrous  $\text{Na}_2\text{SO}_4$  is effective in decreasing the water content of fusel oil and a ratio of 0.15 g  $\text{Na}_2\text{SO}_4$  per  $\text{cm}^3$  of fusel oil is suitable. The same salt/fusel oil ratio was used in this study to decrease the water content of fusel oil. The raw and dried fusel oils were subjected to simple distillation. Approximately 95% of the raw fusel oil was distilled and the residue was discarded. Based on the amount of the distillates collected at the temperature intervals, the distillation curves of both raw fusel oil and dried fusel oil were determined. The results are shown in. The figure indicates that the fractions of the distillates for dried fusel oil collected at lower temperatures are less than those for the raw fusel oil. This indicates that the boiling point of the dried fusel oil increased, since the water in raw fusel oil is essentially removed during  $\text{Na}_2\text{SO}_4$  treatment.

The distillate fractions were analyzed by g.c. as described above. The trend of average compositions of the fractions are also shown in Figure 2. This composition trend is common for both raw and dried fusel oils since it is given on the water-free basis. These data and the g.c. traces suggest that fusel oil can be separated relatively easily into the major three alcohols (ethyl alcohol, i-butyl alcohol, i-amyl alcohols) by simple distillation.

It was estimated that, depending on the desired product, approximately 70% of these major alcohols can be recovered by simple distillation with a purity of 90% or more. However, no attempt was made at this stage to separate or purify the components.



**Figure 2.** Distillation curve of fusel oil and average composition of the distillate fractions depending on the average distillation temperature.

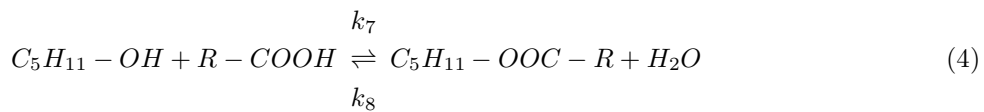
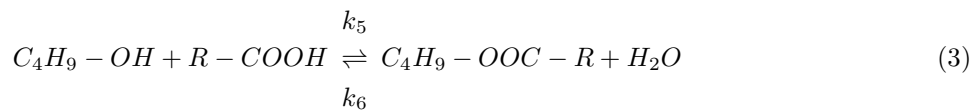
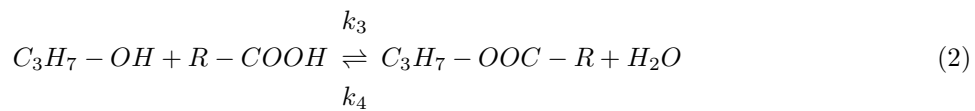
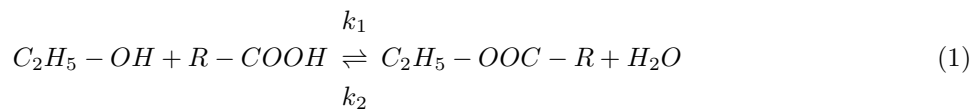
— : Cumulative weight fraction of raw fusel oil.

-.- : Cumulative weight fraction of dried fusel oil.

Average composition of distillate fractions (on water-free basis):  $\Delta$  : ethyl alcohol, o: i-butyl alcohol,  $\bullet$  : i-amyl alcohol.

#### *Esterification of Fusel Oil with Organic Acids*

Since the esters have economic value as chemicals for flavor and fragrance manufacturing, studies on their direct synthesis from major alcohol sources have been received with great interest.<sup>5-8</sup> The data in the literature on the uncatalyzed esterification of fusel oil and its reaction kinetics, however, are very limited.<sup>9</sup> Esterification is a reversible reaction and the esterification of fusel oil may be represented by the set of simultaneous reactions:



where R-COOH is a carboxylic acid, i.e., acetic acid, propionic or butyric acid, R'-OOC-R is their esters and R' is the alkyl group of the alcohols. These reactions are slow and the time to reach equilibrium is relatively

long under mild conditions. Therefore, using a suitable catalyst may substantially increase the reaction rates and conversion ratios. In the esterification of fusel oil, generally, the effective reaction parameters and the effectiveness of lipase enzyme were investigated (5-8). Welsh and Williams<sup>5</sup> reported that in lipase mediated esterification of fusel oil, the maximum production yield of mixed acetic acid esters was 46% and butyric acid ester was 65% in 48 hours. Gilles et.al.<sup>6</sup> reported higher conversions for esterification of alcohols using immobilized lipase enzyme. They also reported that the enzyme activity decreased after one use. This is a significant disadvantage for enzyme mediated esterification. Ghuiba et.al.<sup>9</sup> reported conversions up to 100% in the chemical esterification of fusel alcohols. In this study, the esterification of fusel oil was carried out without externally added catalyst to compare the conversion results with those from the enzyme catalyzed esterification. In some reactions, an equal volume of hexane was added to the reaction mixture to separate the water phase and to move the reactions forward. Due to stirring, however, an effective phase separation was not observed during the reactions and the reaction media was almost homogenous. Only a slight phase separation was observed when stirring stopped after 60 min. of the reaction. Samples were withdrawn from the reaction mixture and directly injected to the gas chromatograph. By using the pure component properties, the modified g.c. data were converted to mol/l concentrations and the results for the reactions at 45 °C are shown in Figures 3-6. The estimated maximum conversions at various reaction times are shown in Table 3. The maximum production yield of the mixed acetic acid esters was 19%, propionic acid esters 24% and butyric acid ester 35% in 6 hours of reaction time. The data in the figures indicate that conversion of fusel alcohols to their esters is slow and it gets slower after approximately 150 minutes of reaction time.

The analyses of the reaction mixtures under reflux conditions exhibited some difficulties and some sampling errors. The mixtures started boil at around 82-83 °C and the samples were withdrawn at temperatures around 80 °C. The samples in the syringe reached thermal equilibrium with room temperature almost instantaneously. The cooled samples may not have an identical composition to the hot reaction mixture. Therefore, the sampling and injection time must be as short as possible. Otherwise, the composition of the samples may change in the meantime, since the reactions are reversible and sensitive to temperature. The compositions of the first fractions of head products (approximately 10 g at a temperatures below 90 °C) were compared after refluxing for approximately 5 minutes and 60 minutes. The uncorrected g.c. results gave approximately 75% ethanol 12% ethyl acetate for the first sample and 60% ethanol 25% ethyl acetate for the second sample. The repeated injections of the same samples, after waiting for approximately 30 minutes at room temperature gave relatively different results from the former analysis. As a result, the real composition of the reaction mixture under reflux conditions could not be determined reliably. However, the head product analyses suggest that conversions are appreciably higher in comparison to the low temperature conversions.

#### *A Kinetic Approach*

Esterification of fusel oil is, in fact, a complex reaction since it involves a set of at least four parallel and reversible reactions. This reaction scheme cannot be handled easily in theoretical investigations. However, based on the experimental data and on some plausible assumptions, some of the kinetic parameters involved in the reactions may be estimated. The following assumptions were made in this investigation:

1. The above reactions 1-4 are second order elementary homogenous reactions and the rate constants for both forward and reverse reactions do not change with time.
2. The reaction mixture does not include water at the beginning. Therefore, the amount of mol of water at any time is equal to the total decrease in the mol of the acid.
3. The unreacted acids are not dissociated.



4. Although the concentrations of some components (amyl alcohol and the acids) are high in the reaction mixtures, the activity coefficients of the components are equal to unity and the equilibrium constant for each reaction can be estimated by applying the law of mass action.
5. The equilibrium constant for a reversible reaction is also equal to the ratio of the rate constants (forward/reverse).

**Table 3.** The maximum conversions of the major alcohol components of fusel oil or the reacting acids into esters in 6 hours of reaction time.

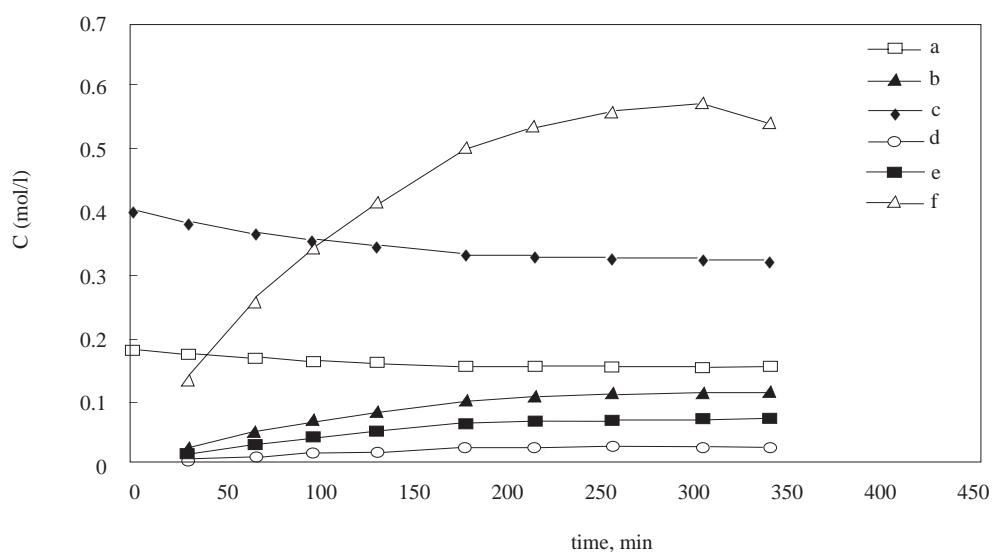
Reactive (alcohol/acid)	time (min)	Acetic acid	Propionic acid	Butyric acid
ethyl alcohol	30	3.0	3.7	4.0
	60	5.9	7.2	8.1
	300	13.5	16.2	25.0
propyl alcohol	30	3.4	4.2	5.7
	60	6.8	8.1	8.1
	300	15.6	18.7	27.5
i-butyl alcohol	30	4.0	4.2	4.0
	60	7.8	8.2	8.1
	300	17.5	20.8	27.8
i-amyl alcohol	30	5.0	5.8	6.0
	60	8.6	9.9	10.1
	300	20.2	24.3	35.0
the acids	30	4.6	5.3	6.4
	60	9.0	10.5	10.1
	300	19.8	21.5	35.0

If the reactions were second order irreversible (or the reverse reactions were neglected at very beginning), the following simple equation can be used to estimate the rate constant for each reaction.

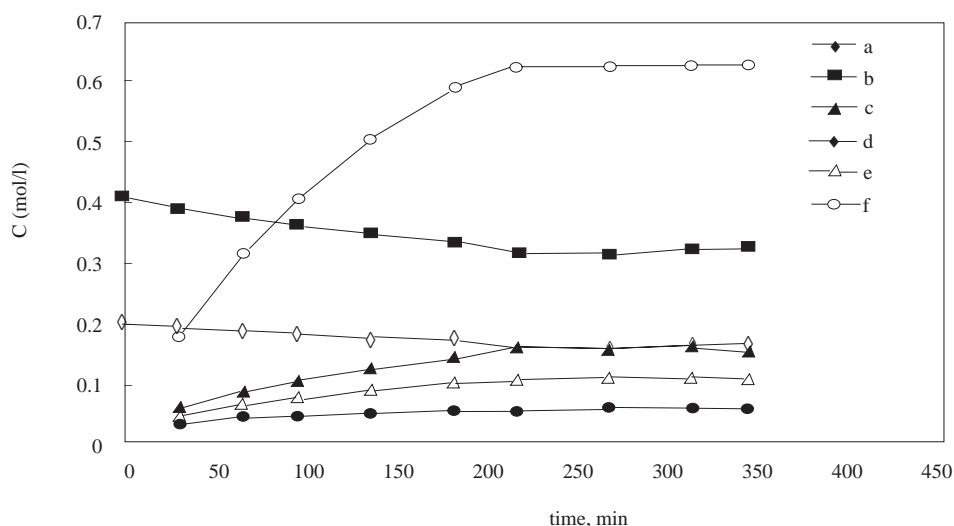
$$\frac{dX}{dt} = k(a - X)(b - X) \quad (5)$$

where  $a$  and  $b$  are the initial concentrations of alcohol and acid respectively.  $X$  is the ester formed after the reaction time  $t$ . The  $k$  values for each reaction may be estimated by approximating  $dX/dt$  as  $\Delta X/\Delta t$  since the instantaneous concentrations of the reactants are determined. The results for approximately the first 90 minutes of the reaction are given in Table 4. It can be seen from the table that the rate constants decrease regularly with time. This is an expected result since the reactions are reversible and the “ $k$ ” values in the table at ( $t > 0$ ) do not represent the real rate constants, but may be assumed to be the apparent constants. The real rate constants for the forward reactions may be estimated by extrapolating the apparent rate constants to the zero reaction time. The rate constants estimated in this manner are shown as  $k_0$  in Table 4. The results in the table indicate that the estimated constants are relatively small. Such small rate constants are conceivable since the acids used are weak acids (their dissociation constant in aqueous solutions is around  $pK_a = 4.8-4.9$ ). Although acetic acid is slightly stronger than the others, its esterification reaction seems to be the slowest. Similar conclusions have also been drawn for the lipase mediated esterifications.<sup>5-8</sup> This result suggests besides strength, an acid and some other parameters of the acid (such as molecular size and steric effects) also affect the rate of esterification.

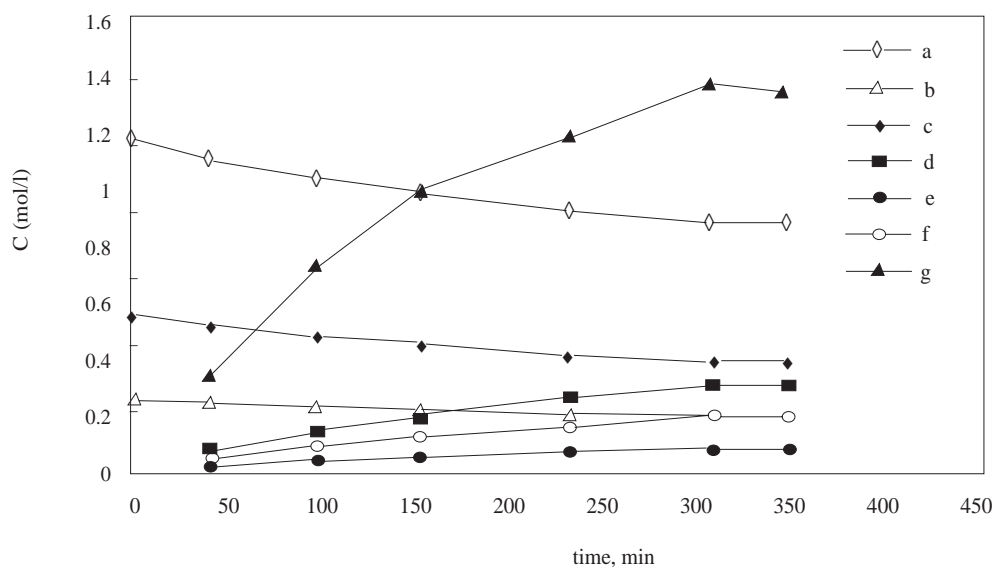
The data in Figures 3-6 indicate that the compositional change is very slow after 330 minutes of the reaction. Therefore, it may be assumed these concentrations represent the end of the reactions. If this is valid, the deviation from the equilibrium is infinitesimal, as in quasi-equilibrium. Based on the above mentioned assumptions, the equilibrium constants for reactions 1-4 are estimated. The results for esterification reactions with acetic acid, through reactions 1-4 are  $K_d(1) = 0.037$ ,  $K_d(2) = 0.043$ ,  $K_d(3) = 0.052$  and  $K_d(4) = 0.066$ , respectively. The corresponding constants for the esterification with propionic acid are  $K_d(1) = 0.054$ ,  $K_d(2) = 0.062$ ,  $K_d(3) = 0.073$  and  $K_d(4) = 0.090$  and with butyric acid are  $K_d(1) = 0.185$ ,  $K_d(2) = 0.212$ ,  $K_d(3) = 0.265$  and  $K_d(4) = 0.382$ . In fact, each reaction has its characteristic equilibrium constant.



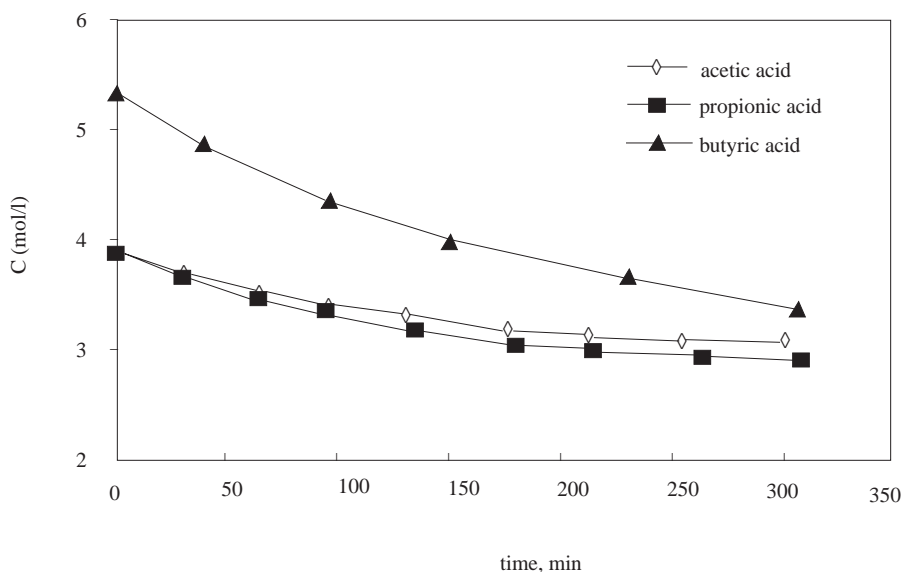
**Figure 3.** Compositional changes for the alcohols and the esters with time in the reaction of the fusel oil with acetic acid. a: propyl alcohol, b: ethyl acetate, c: i-butyl alcohol, d: propyl acetate, e: i-butyl acetate, f: i-amyl acetate.



**Figure 4.** Compositional changes for alcohols and the esters with time in the reaction of the fusel oil with propionic acid. a: propyl alcohol, b: i-butyl alcohol, c: ethyl propionate, e: i-butyl propionate, d: propyl propionate, f: i-amyl propionate.



**Figure 5.** Compositional changes for alcohols and the esters with time in the reaction of the fusel oil with butyric acid (reaction mixture was not diluted with hexane). a: ethyl alcohol, b: propyl alcohol, c: i-butyl alcohol, d: ethyl butyrate; e: propyl butyrate, f: i-butyl butyrate, g: i-amyl butyrate.



**Figure 6.** Changes over time in the concentrations of the acids during the reaction.

However, one may expect the equilibrium constants to be similar for each component, under identical conditions since the acids used in the reactions are similar. The different  $K_d$  values with different acids imply that thermodynamic equilibrium is not established especially for acetic or propionic acid reactions within 330 minutes. However, these  $K_d$  values still may be used as a reference since the compositional change is very slow after this time. The estimated rate constants for the forward reactions (the  $k_0$  values) may be used for a comparison of the relative reaction rates. The lower conversion values and lower  $K_d$  values for ethyl alcohol and propyl alcohol may be a result of their lower initial concentrations. A relatively

higher amount of water was formed during esterification of i-amyl alcohol since the initial concentrations were higher. This water suppresses the conversion of the alcohols with low concentration.

The rate constants for the reverse reactions may be estimated by dividing K<sub>d</sub> values by related k<sub>0</sub> values. However, these values may not be reliable since both k<sub>0</sub> and K<sub>d</sub> values are subject to error. Nevertheless, the above data suggests that the rate constants for reverse reactions are higher than for the forward reactions. This conclusion implies that an effective phase separation does not take place in the course of the reaction, in order to shift the reactions in favor of formation of the esters.

## Conclusions

Fusel oil includes mainly three alcohols: ethyl alcohol, i-butyl alcohol and i-amyl alcohols. Various unpleasant properties of fusel oil may be removed and a substantial portion of the major alcohol components can be separated by simple distillation. These alcohols can be used as solvents or several mixed esters can also be prepared for various other purposes. The handling and utilization of distilled fusel oil or the recovered alcohols, is easier and has several advantages over raw fusel oil. The fusel oil, the alcohols and the esters are valuable chemicals and can be used for extraction or other purposes. Butyric ester conversion is higher than acetic or propionic acid esters. However, the rate of conversion of fusel alcohols to their esters through simple chemical reactions, in general, is very low in comparison with enzyme catalyzed esterification. The continuous removal of water or ether from the reaction media may increase the conversion ratios. The results of this study emphasize that fusel oil is a valuable chemical raw material and there are several alternative ways of utilizing it. Further studies must be carried out to increase the ester conversions through the chemical reaction and to separate the products.

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