SEPARATION 2-methylbutan-1-ol a 3-methylbutan-1-ol FROM FUSEL OIL

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Abstract

These work was focused on the isolation of 3-methylbutan-1-ol and 2-methylbutan-1-ol from fusel oil by distillation. We make separation of two different fusel oils from bioethanol fermentation in packed rectification columns. The aim was to obtain 99 % purity of isoamyl alcohol (3-methylbutan-1-ol) and active amyl alcohol (2-methylbutan-1-ol).

Keywords: *distillation, fusel oil, reflux ratio, F-factor*

1. INTRODUCTION

Fusel oil is produced as a by-product in fermentation processes. It is a mixture of higher alcohols such as propanols, butanols, pentanols, but the most are amyl alcohols such as isoamyl alcohol (3-methylbutan-1-ol) and active amyl alcohol (2-methylbutan-1-ol). Both ethanol and fusel compounds are toxic to yeast growth and fermentation, but fusel compounds are 10 to 15 times more toxic to yeast than ethanol. Removing fusel compounds properly is accomplished using a rectification column, which adds capital, energy and operating cost. By adjusting the pressure, flow and operating temperature in the rectification column, the fusel compounds are removed from the ethanol via draw points on the side of the column and a fusel draw pump.

Ferreira el all. [1] presented the study aimed to evaluate the industrial distillation process of fusel oil to obtain isoamyl alcohol using the Aspen Plus simulator. An extensive literature on the aspects of composition, removal and potential utilization of fusel oil is reviewed [2,3]. The paper mainly focuses on fusel oil of cane molasses origin and the utilization aspects are classified under separate sections. The interest in alternative fuels is increasing globally to reduce dependence on fossil fuels [4]. In HCCI engines, it is possible to control the combustion process with high octane fuels also by adding fusel oil. In [5] two distillation schemes for obtaining isoamyl alcohol from fusel oil is proposed: a conventional distillation sequence and a dividing wall column. After validation of thermodynamic models to accurately describe phase equilibria of fusel components, and dividing wall column (DWC) separation scheme was developed. Both traditional sequential distillation and DWC system were optimized.

Component	Maize	Sugar cane
	%	%
Ethanol	3,22	0,8
Propan-1-ol	0,53	0,17
Isobutanol	17,50	13,1
Butan-1-ol	0,08	0,24
Isoamylalcohol	60,64	78,9
Water	16,62	3,8
Residual	1,43	3,0

Table 1. Fusel oil from fermentation of maize and sugar cane [6].

The fusel oil samples from two bioethanol plants, from maize fermentation and sugar cane fermentation is summarized in Table 1. It can be observed that isoamyl alcohol, water, isobutanol, and ethanol are the major compounds.

Due to the presence of water in fusel oil, heterogeneous azeotropes form between water and most of the higher alcohols. In Table 2 are presented azeotropes of several components of fusel oil with water.

Alcohol	Azeotrop	
	Boiling point [°C]	Weight % of water
Ethanol	78,15	4,0
Isopropanol	80,3	12,6
Propan-1-ol	87,0	28,3
Butan-2-ol	87,5	27,3
Isobutanol	89,8	33,0
Butan-1-ol	92,7	42,5
Isoamylalcohol	95,2	49,6
Hexan-1-ol	97,8	75,0

Table 2. Azeotropes of several components of fusel oil with water [7].

Component	Boiling point [°C]	Molecular weight [kg.kmol^{-1}]	Density 20°C [kg.m^{-3}]
3-methylbutan-1-ol	131-132	88,15	812
2-methylbutan-1-ol	128	88,15	816
Ethanol	78,3	46,07	789
Propan-1-ol	97,2	60,10	804
Propan-2-ol	82,3	60,10	786
2-methylpropan-1-ol	107,8	74,12	803
Butan-1-ol	117,8	74,12	810
Hexan-1-ol	157	102,18	820

Table 3. Some physical data of fusel oil components.

2. MATERIALS AND METHODS

2.1. Fusel oil No.1

Analysis of fusel oil No.1 shows the presence approx. 109 components and water, which was not detected by chromatograph. We identified 16 components, which together makes up 98,7%, rest makes only 1,3 %. The results of analysis are presented in Table 4.

Component	Retentive time [min]	% area
Acetone	1,793	0,004
Ethylacetat	2,108	0,007
Ethanol	2,473	1,925
Propan-1-ol	3,633	0,022
2-methylpropan-1-ol	4,553	0,215
Butan-1-ol	5,703	0,227
3-methylbutan-1-ol + 2-methylbutan-1-ol	8,064	94,401
Pentan-1-ol	8,687	0,069
2-methyltetrahydrofuran-3-on	8,840	0,300
Heptan-2-ol	11,207	0,151
Hexan-1-ol	12,300	0,159
Ethyl-octanoat	15,144	0,260
Ethyl-decanoat	22,726	0,747
β-damascenon	28,329	0,041
Ethyl-dodecanoat	29,801	0,179

Table 4. Analysis of components in fusel oil No. 1

2.2. Fusel oil No. 2

The analysis showed the presence of 60 components and water, which was not detected by chromatograph. We identified 15 components which was 98,47%, the rest 45 components was only 1,53%. The components identified in fusil oil No. 2 are presented in Table 5.

Component	Retentive time [min]	% of area
Acetone	1,792	0,011
Ethanol	2,474	4,426
Propan-1-ol	3,633	0,677
2-methylpropan-1-ol	4,557	2,026
Butan-1-ol	5,698	0,286
3-methylbutan-1-ol + 2-methylbutan-1-ol	7,827	89,259
Pentan-1-ol	8,760	0,127
2-methyltetrahydrofuran-3-on	8,792	0,141
Heptan-2-ol	11,171	0,177
Hexan-1-ol	12,267	0,144

Ethyl-oktanoat	15,105	0,237
Ethyl-decanoat	22,667	0,732
β-damascenon	28,311	0,057
Ethyl-dodecanoat	29,763	0,167

Table 5. Fusel oil No. 2

2.3. Rectification

The glass column was from Sulzer company, with packed bed 1,49 m, diameter of column 0,04 m, packed bed was filling with 27 elements of EX segment (0,055 m each) Fig.1 It allows highest possible number of theoretical stages, even with very low liquid loadings. This packing is suitable for laboratory columns where a modest number of theoretical stages is required, together with low pressure drop and high capacity. The column was isolated, with possibility of heating and temperature measurement. On the top and at the bottom of the bed we measured pressure drop. During distillation the temperature and the pressure in the column, the temperature on the top and at the bottom of column, the pressure in the column, the temperature of isolation, the pressure drop in the column was measured and registered.



Fig. 1. Filling Sulzer EX

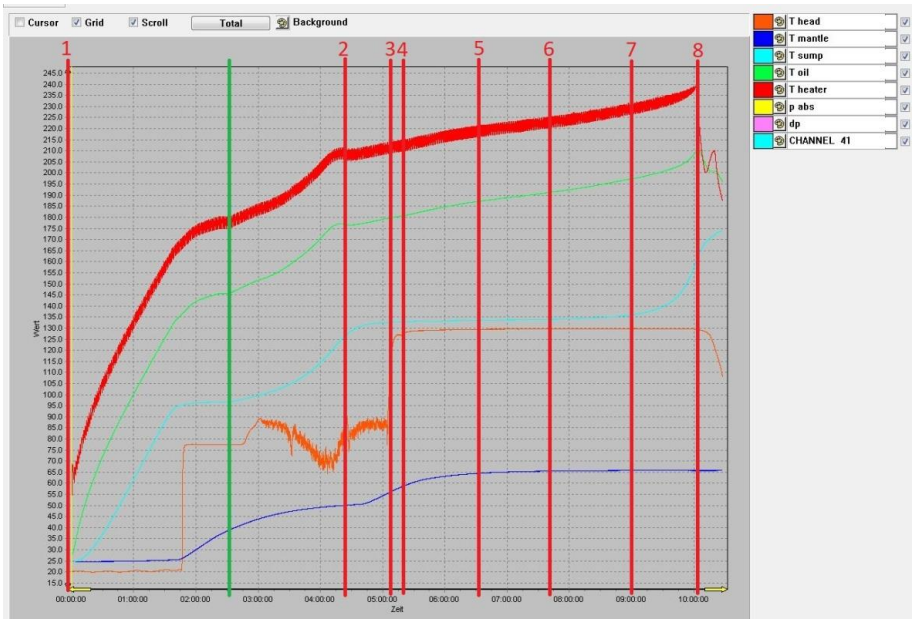


Fig. 2. The registered parameters during rectification; fusel oil No.2, reflux ratio 10:1

3. RESULTS AND DISCUSSION

3.1. Rectification of fusel oil No.1

Fusel oil No.1 was distillated at the reflux ratio 2:1, 3:1 and 10:1. We received the purity of 3-methylbutan-1-ol a 2-methylbutan-1-ol mixture more than 90 % in 5 fractions. The results show that for receiving 99% concentration of this mixture, the reflux ratio 3:1 is sufficient. The best results we obtained at the reflux ratio 10:1, but distillation time and energy consumption are higher.

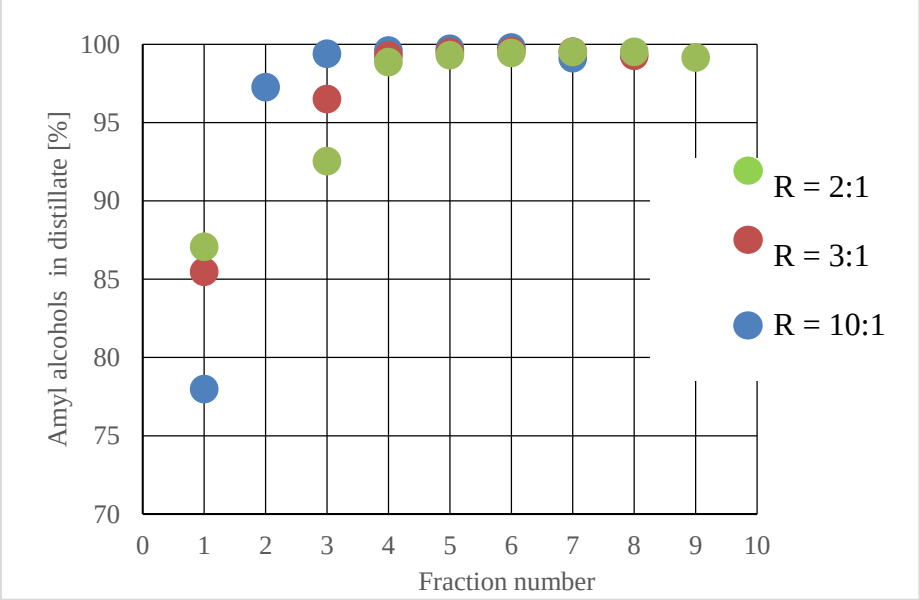


Fig. 1. Rectification of fusel oil No. 1

3.2. Rectification of fusel oil No.2

Fusel oil No. 2 was rectified at the reflux ratio 2:1, 3:1, 5:1 and 10:1. The results are presented in Fig.4. We achieved the concentration of 99 % of 3-methylbutan-1-ol a 2-methylbutan-1-ol at the reflux ratio

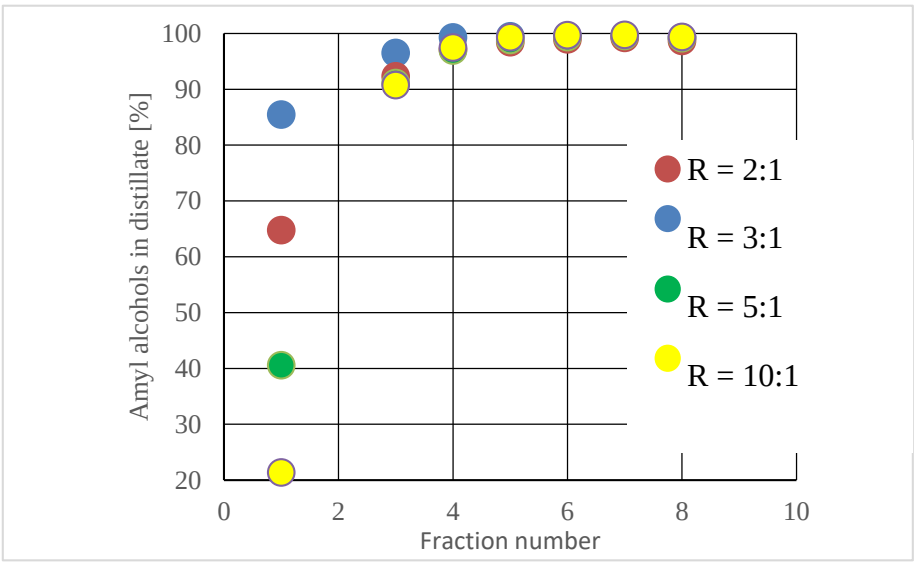


Fig. 2. Rectification of fusel oil No. 2

5:1 already after 3 fractions with their volume yield 27,9 %. The best results, we achieved at reflux ratio 10:1 when fractions comprising 99 % 3-methylbutan-1-ol a 2-methylbutan-1-ol provided 49,9 % yield. But at this reflux ratio is highest expenditure of energy.

3.3. F factor

Flooding factor can be calculating from

$$F = w_V \sqrt{\rho_V}$$

Where w_v is vapor velocity in free column, ρ_v is vapor density.

Calculated values of F factor are presented in Table 6. The values of F factor were in the range from 0,13 to 0,51 $\sqrt{Pa}$, which corresponds HETP (height equivalent theoretical plate) from 0,015 to 0,025. (except fraction 7 and 8 in several reflux). This confirm that column worked with the highest efficiency. Fig. 5.

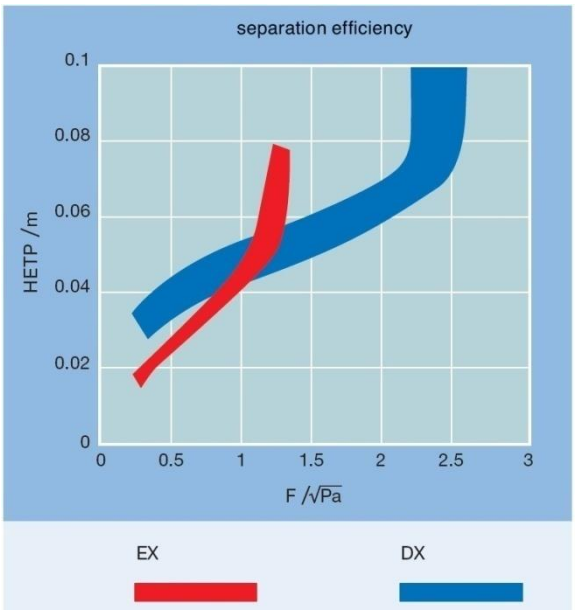


Fig. 5. HETP versus F-factor (red color for filling EX) [8]

	Fusel oil 1			Fusel oil 2		
Reflux ratio	2:1	3:1	2:1	3:1	5:1	10:1
Fraction	F [$\sqrt{Pa}$]					
FR4	0,43	0,45	0,44	0,43	0,45	0,51
FR5	0,36	0,35	0,43	0,48	0,50	0,53
FR6	0,26	0,28	0,35	0,41	0,48	0,51
FR7	0,23	0,24	0,13	0,24	0,33	0,48
FR8	0,11	0,04	0,03	0,06	0,06	0,16
FR9	0,05	-	-	-	-	-

Table 6. Calculated values of F-factor

4. CONCLUSION

After the analysis of two types of fusel oils, we studied the separation of 3-methylbutan-1-ol a 2-methylbutan-1-ol in packed bed rectification column. Our aim was to obtain 99% concentration of this mixture. The results showed that for fusel oil No.1 the reflux ratio 3:1 is sufficient, for fusel oil No.2 the reflux ratio 5:1 is sufficient.

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