PRODUCTION OF SELECTED COMPOUNDS FROM FUSEL OIL

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Abstract

The aim of this work was to propose a technology for effective separation of two isomers of butanol (3-methyl butan-1-ol and 2-methyl butan-1-ol) from the multi-component mixture „fusel oil", which is a byproduct of ethanol production via fermentation. Requirements for this separation are to achieve high degree of purity (99%+) and the highest reasonably possible yield. Additionally, we were requested to avoid the use of any additional substances, as the final product is supposed to be natural. Fusel oil sample from industrial mill was analyzed by gas chromatography. Batch rectification of fusel oil was used for this purpose. Experiments were realized on laboratory distillation packing column under various reflux ratio. Simulation calculations were done using Aspen Plus simulator with thermodynamic model UNIQAC for vapor-liquid equilibria. Results of mathematical modelling are very close to the experimental data.

Keywords: *Fusel oil, distillation, amyl alcohols, reflux ratio, F-factor*

INTRODUCTION

Agro-industrial waste is a valuable resource not only in the search for renewable sources of energy but they can be used for production of high added-value substances too. Typical liquid waste from this sector of industry is fusel oil (also known as fusel alcohol). Fusel oil is a mixture of many compounds obtained as a side cut during ethanol distillation mainly composed of methanol, ethanol, water and higher alcohols (C3-C5). Production of ethanol as renewable fuel or source of energy is realized mainly by fermentation. All higher alcohols are side products generated during ethanol biosynthesis, so the nature and quantity of fusel oil produced depends largely on type of fermented biomass, fermentation operating conditions and its performance.

Fig. 1 shows global ethanol production by country, from 2007 to 2019 [1]. Global production continues to increase. The United States is the world's largest producer of ethanol. Together, the United States and Brazil produce 84% of the world's ethanol. The vast majority of U.S. ethanol is produced from corn, while Brazil primarily uses sugarcane.

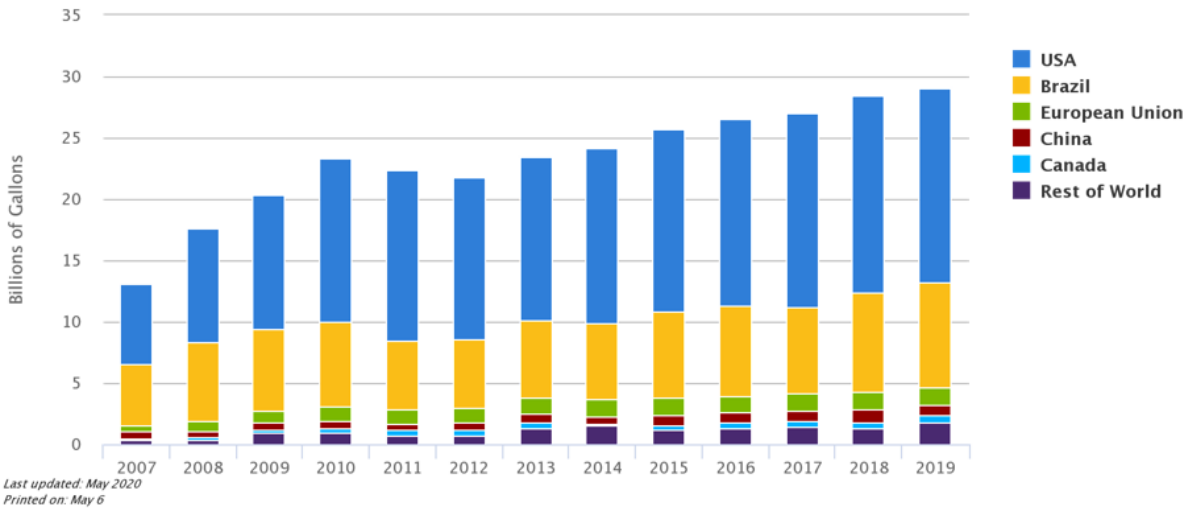


Fig. 1. Ethanol production by country from 2007 to 2019 [1].

As can be seen from Fig.1 the world's ethanol production now is about 100 billion of liters per year. If we take into account production of fusel oil on the level 1-11 L per each 1000 L of ethanol [2], we have much more than 100 million L of fusel oil per year. Because of the low production volume compared with ethanol, fusel oil has been considered as liquid waste, and it has been generally used as an energy source within the distilleries.

A valorization alternative for fusel oil could be the purification and esterification of alcohols. Esters from C2 to C8 alcohols are widely used at the industrial scale as a high value-added flavor and fragrance components for food, beverage, cosmetic and pharmaceutical industries [4]. Specifically, isoamyl acetate is extensively used as "green solvent" (methyl ethyl ketone substitute), as an additive in nitrocellulose lacquers, and as banana- or pear-like flavoring agent [3].

For obtaining above mentioned chemicals it is necessary first to separate target higher alcohols from fusel oil. In our contribution we focused on the separation of two isomers of butanol: 3-methyl butan-1-ol (isoamyl alcohol) and 2-methyl butan-1-ol (active amyl alcohol). On this project we cooperated with one private company in Slovakia, which produces natural aromatic substances. Requirements for this separation are to achieve high degree of purity (99+ %) of both isomers, with as high yield as reasonably possible. Additionally, we were requested to avoid the use of any extraneous substances, as the final product is supposed to be marketed as „natural". In addition to a proposal of a technological procedure, this work also contains a comparison of computer simulations with experimental data. The technological procedure itself contains several steps, starting from raw fusel oil as a feed and resulting in pure mixture of isomers as product.

MATERIALS AND METHODS

For experimental measurements we had at the disposal the fusel oil derivable from fermentation of molasses. For analysis of organic components contained in the fusel oil was used gas chromatograph 7890B with MSD detector type 5977B (Agilent technologies). For water content in the fusel oil Karl Fischer titration was used.

The glass column used for distillation experiments was made by company Sulzer. We had possibility to run distillation as batch rectification process with feasibility to adjust heating power, reflux ratio and pressure inside the column. Distillation column was filled with packed bed 1,49 m height; column diameter was 0,04 m. Packed bed consisted of 27 elements of very efficient laboratory packing segment type EX (0,055 m each). The column was thermally isolated, with possibility to heat up isolation and temperature measurement. At the top and bottom of packed bed we measured pressure drop. During distillation process the temperature and pressure in column, temperature at the top and bottom of the column, temperature inside isolation and pressure drop in the column were measured and registered in data acquisition system.

We filled up 3000 ml of fusel oil to electrically heated reboiler equipped with oil bath (filled with MARLOTHERM) and run of distillation process was then controlled automatically. We obtained totally 8 fractions of distillate with volume approximately 500 ml each. Experiments were done under atmospheric pressure with reflux ratio R=2, 3, 5 and 10 respectively. Experimental equipment is depicted in Fig. 2.



Fig. 2. Experimental column used for batch rectification of fusel oil.

As it was mentioned above, pocked bed of type EX from Sulzer company had very high separation efficiency. This is well documented by following Fig. 3, where is depicted HETP (Height equivalent to a theoretical plate) as a function of F-factor (flooding factor).

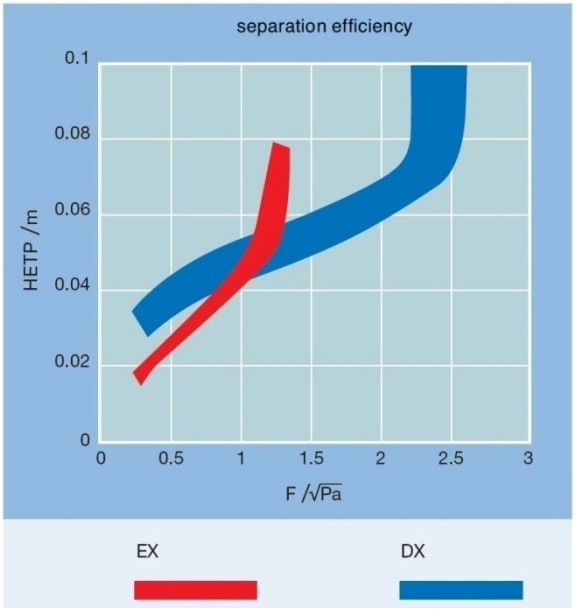


Fig. 3. HETP versus F-factor (red color for packing EX) [5]

F-factor is defined as the product of the superficial vapor velocity and the square root of vapor density and is based on the column bottom or head conditions.

$$F = w_g\sqrt{\rho_g} \quad (1)$$

w_g is the average velocity of vapor in free cross section of distillation column

ρ_g is the density of vapor inside the column.

As can be seen from equation (1) value of F-factor depends on hydrodynamic conditions inside the distillation column. Continuance of distillation process we adjusted by changing heating power in reboiler in order for F-factor had value between 0,5-1.

RESULTS AND DISCUSSION

Results of fusel oil analysis are aforementioned in Table 1.

In the Table 1 AA (amyl alcohols) is the sum of 2-methyl butan-1-ol and 3-methyl butan-1-ol, it means both amyl alcohols together. The latter isomers of butanol have very similar physical and chemical properties and used GC column was not able to differentiate them. But for our needs it was sufficient, because our target is separation of above mentioned isomers of butanol from fusel oil.

Because many of components of fusel oil are creating azeotropic mixtures with water, second column in Table 1 lists boiling point temperature of these azeotropic mixtures under atmospheric pressure.

Finally, 14 components of liquid mixture are too many for simulator Aspen Plus we used for calculations. For some components there are no data for liquid-liquid and vapor-liquid equilibrium in the database of Aspen Plus. Consequently, we had to make simplification and reduce number of components to 9. We affiliated hexanol and heptan-2-ol to one component with properties of hexanol and all heavy compounds as ethyl octanoate, ethyl decanoate, β-damascenone, ethyl dodecanoate and the rest of heavy compounds are represented as ethyl octanoate. Composition of reduced 9 component mixture is listed in the column on the right side of the Table 1.

Table 1. Composition of fusel oil (AA = amyl alcohols).

Component	**Weight [%]**	**$T_{bp,az}$ [°C]**	**Component**	**Weight [%]**
Ethanol	4,12	78,2	Ethanol	4,12
Propanol	0,63	87,7	Propanol	0,63
Isobutanol	1,89	90,3	Isobutanol	1,89
Butanol	0,27	92,6	Butanol	0,27
AA	83,01	94,2-95	AA	83,01
Pentanol	0,12	96,4	Pentanol	0,12
Hexanol	0,13	98	Hexanol	0,30
Heptán-2-ol	0,17	100		
Ethyl octanoate	0,22	-	Ethyl octanoate	2,66
Ethyl decanoate	0,68	-		
β-damascenone	0,06	-		
Ethyl dodecanoate	0,16	-		
The rest of heavy comp.	1,54	-		
Water	7,00	-	Water	7,00

Typical continuance of one distillation process is adduced in Fig. 4.

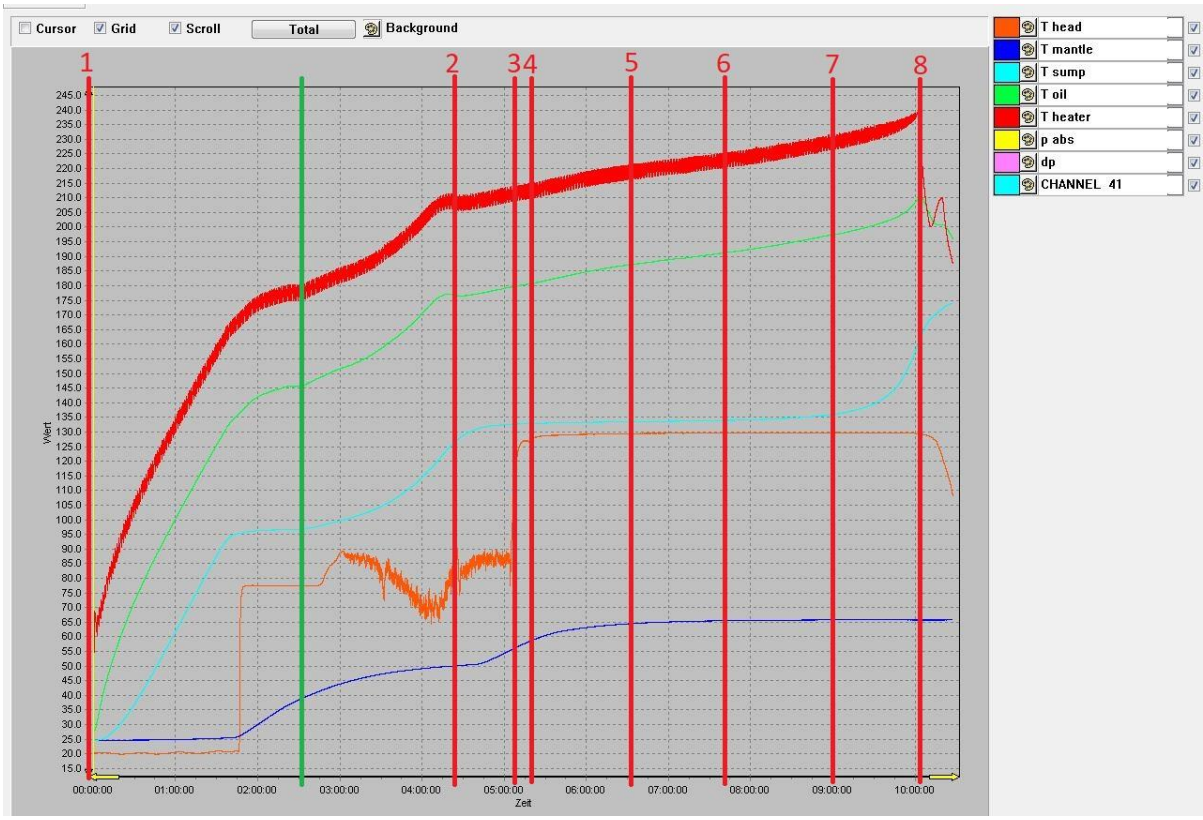


Fig. 4. Continuance of fusel oil distillation: atmospheric pressure, reflux ratio 10:1.

From the Fig. 4 one can see same interesting facticity. Vertical green line means starting of distillate withdraw. Next vertical red lines depict moment, when collection of previous fraction of distillate finished and next fraction started.

From the separation point of view, the most important is temperature on the top of distillation column, in Fig. 4 orange line marked as T head. From the beginning distillation column is heated up and no distillate is collected, it means rectification runs with infinity reflux ratio. Then first and second fractions collected mainly light components from fusel oil and azeotropic mixtures with distillation temperature range 70-90°C. Third fraction is transient, it started when temperature T head sharply increased to 125°C. Next fractions are so called production fractions; they comprise mainly amyl alcohols. Temperature T head was constant on the level of 130°C. It means, that amyl alcohols distilled in this period. After that distillation was stopped, then we measured the volume of each fractions and the distillation rest and take probes of individual fractions for analysis. Results of measurements are listed in Table 2.

Table 2. Comparison of experimental and simulated data for reflux ratio R=5, [6].

			Experiment		**Simulation**	
	τ_{FR}	R	V_{FR}	w_{AA}	V_{FR}	w_{AA}
	[min]		[ml]	[-]	[ml]	[-]
Raw material	-		3000	0,888	3000	0,888
FR1 - VF	99	10	134	-	145	0,067
FR1 - OF		10	580	0,406	579	0,717
FR2	19	10	154	0,911	157	0,917
FR3	47	5	535	0,966	530	0,962
FR4	41	5	510	0,988	509	0,985
FR5	42	5	510	0,994	509	0,993
FR6	36	5	300	0,995	300	0,992
FR7	17	5	27	0,992	27	0,989
DZ	-		200	0,533	303	0,708

In the Table 2 we can see both experimental and simulated data. OF/VF means organic/water phase.

V_{FR} is the volume of each fraction

w_{AA} is the weight fraction of amyl alcohols

τ_{FR} is the time duration of acquirement adduced volume of each fraction

R is the reflux ratio.

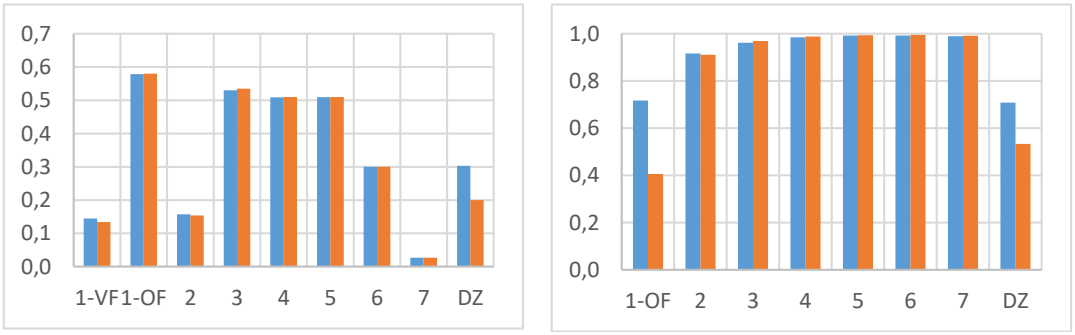


Fig. 5. Fraction volumes (left) and weight fraction of amyl alcohols within fractions (right) for R=5, orange = experiment, blue = calculated, DZ= distillation rest.

In the Fig. 5 we can see comparison of experimental and calculated values in graphical way for R = 5. Good agreement between fraction volumes calculated and experimentally measured was obtained besides rest of distillation. It can be caused by mixing volume contraction and/or dilatation due to not ideal behavior in liquid phase or by integration mistake in the simulator.

Calculated and measured concentrations of amyl alcohols shows good accordance too, besides first fraction and rest of distillation. First fraction was divided to organic and water phase and amyl alcohols inside the water phase was not measured. Probably this is the reason of above mentioned difference. In the distillation rest the disagreement in concentration values could be caused by volume difference as

we mentioned before. If the volume of DZ is not correct, from the material balance we calculate wrong concentration of amyl alcohols.

Representation of distillation results for other reflux ratios are very similar to presented one. It is clear from the next table 3.

Table 3. Comparison of experimental data for various reflux ratios.

	R = 2		**R = 3**		**R = 5**		**R = 10**	
	V_{FR}	w_{AA}	V_{FR}	w_{AA}	V_{FR}	w_{AA}	V_{FR}	w_{AA}
	[ml]	[-]	[ml]	[-]	[ml]	[-]	[ml]	[-]
Raw material	3000	0,893	3000	0,893	3000	0,888	3000	0,892
FR1 - VF	154	-	140	-	134	-	0	-
FR1 - OF	579	0,648	595	0,497	580	0,406	687	0,214
FR2	224	0,923	184	0,918	154	0,911	43	0,907
FR3	515	0,972	530	0,970	535	0,970	515	0,975
FR4	515	0,984	515	0,986	510	0,988	510	0,993
FR5	515	0,989	510	0,991	510	0,994	530	0,997
FR6	228	0,992	162	0,993	300	0,995	402	0,998
FR7	28	0,987	56	0,991	27	0,992	54	0,994
DZ	208	0,537	214	0,564	200	0,533	200	0,520

What we can see from Table 3 is increasing of separation efficiency with higher reflux ratio. It can be indeed expected. In the case of R=10 we have 4 fractions of distillate with concentration of amyl alcohols more than 99%. Against this, when value R=2 we obtained only one fraction of distillate with so high concentration of amyl alcohols. But we pay for it with time spent for distillation and therefore we have higher operating costs. Distillation time with R=10 was approx. 3-times higher in comparison with R=2.

As was mentioned above, our target is to separate the mixture of amyl alcohols (3-methyl butan-1-ol and 2-methyl butan-1-ol) from fusel oil with summary concentration higher than 99% with maximal possible yield. Using data from Table 3 we calculated values of average concentration and yield of amyl alcohols in the case we combine fractions of distillate from FR4 to FR7. Results are depicted in following Table 4.

Table 4. Average concentration and yield of amyl alcohols (AA) in case of combined fractions FR4-FR7.

Reflux ratio	**R = 2**	**R = 3**	**R = 5**	**R = 10**
AA average concentration [%]	98,75	98,92	99,19	99,58
Yield of AA [%]	47,4	45,9	50,2	55,7

If we take to combine distillate fraction FR3 too, we obtain results listed in Table 5.

Table 5. Average concentration and yield of amyl alcohols (AA) in case of combined fractions FR3-FR7.

Reflux ratio	**R = 2**	**R = 3**	**R = 5**	**R = 10**
AA average concentration [%]	98,30	98,34	98,57	99,05
Yield of AA [%]	66,1	65,1	69,6	74,4

As can be seen in Table 4 and Table 5 amyl alcohols yield is rising with higher reflux ratio. Average concentration of amyl alcohols is higher too if we collect fractions FR4-FR7. There is more than one possibility how to arrange result of distillation process. One is to collect fractions FR4-FR7 obtained with reflux ratio R=5. To avoid the loos of amyl alcohols fraction FR3 and/or FR2 can be recirculated to next distillation process. Another possibility is to realized distillation process with reflux ratio R=10, to collect FR3-FR7 and fraction FR2 with amyl alcohols content on the level 90,7 % recirculate to next distillation process to avoid loos of amyl alcohols. In both cases we obtain cumulative distillate with concentration of the amyl alcohols more than 99 %. But in the case of R=10 we shall have more energy demand comparison to R=5. Optimization of economy balance can answer the right conditions for running distillation process.

CONCLUSIONS

In present article we are concerned with experimental measurement and mathematical modelling of amyl alcohols (3-methyl butan-1-ol and 2-methyl butan-1-ol) separation from fusel oil. Experiments were realized on the packed distillation column with approx. 50 theoretical plates showed, that batch rectification is suitable way to separate both above mentioned isomers of butanol from fusel oil with concentration of distillate more than 99 %, which is suitable for next processing. Reflux ratio for rectification process has to be on the level 5<R<10, for detail specification it is necessary to do economic optimization. Using solver Aspen Plus with therodanamic model UNIQAC we obtained very good agreement between experimental and calculated values for both volume fraction and concentration of amyl alcohols.

ACKNOWLEDGMENTS

This work was supported by the Slovak Research and Development Agency under the contract APVV-17-0109.

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