

Cleaner Process and Entrainer Screening for Bioethanol Dehydration by Heterogeneous Azeotropic Distillation

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Greenhouse gas footprint of fuels is due to both the burning fuel and its production process. Bioethanol is a sustainable biofuel but it is obtained diluted in water and its dehydration consumes large amounts of energy. Heterogeneous azeotropic distillation is a well-known suitable option for dehydration of bioethanol (separation of ethanol from water). Many entrainers for this process are studied in literature but unfortunately, there is no critical comparison in terms of the corresponding process efficiency. The distillation efficiency assessment is necessary as it has a great impact on the energy consumption and sustainability of bioethanol production. The process scheme and entrainer are screened following a fast-to-rigorous procedure: feasibility checking using the infinite/infinite analysis, screening based on the Distillation Sequence Efficiency (DSE) method and rigorous simulation using AspenPlus®. Different process schemes are assessed taking into account also that some gasoline additives, used as entrainers, could remain in bioethanol, which is to be included in the gasoline formulation. Some examples of commonly used ethers as gasoline additives are methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), diisopropyl ether (DIPE) and tert-amyl methyl ether (TAME). The study shows that when the entrainer is a gasoline additive, collecting the distillation product as a mixture of ethanol and additive consumes 27 % less energy than collecting pure ethanol. Performing the ethanol dehydration and gasoline additive mixing together in the same process leads to a 27 % decreasing of CO₂ emissions.

1. Introduction

To reduce the greenhouse gas emissions produced by the transportation sector, the mixture of biomass derived fuels with fossil fuels has been promoted by governments legislative initiatives, e.g. bioethanol mixed in gasoline. There is an intense research to produce bioethanol from lignocellulosic biomass (Rezania et al., 2020). Bioethanol obtained by biomass microbial fermentation is rather diluted in water, i.e. in the range of 5 – 12 % wt ethanol, and according to the current international bioethanol standards, the maximum allowed water content in fuels is 0.3 % wt. in Europe (EN 15376, 2011). Second generation ethanol is obtained even more diluted at concentrations around 50 g/L (Roukas et al., 2020). Bioethanol can be easily integrated into the existing fuel pool as a 5 – 85 % mixture with gasoline without any modification of current engines (Kiss and Suszalak, 2012). Due to the higher content of oxygen in ethanol, it has been used as an oxygenate additive into gasoline pool, which not only leads to a more efficient combustion but also improves the antiknock properties (Cardona and Sánchez, 2007). Bioethanol is also used as raw material to produce gasoline additives, e.g. ETBE and bioethanol dehydration process can be combined with the ETBE synthesis (Li and Liu, 2018).

A binary azeotrope in the water + ethanol mixture makes it impossible to separate ethanol and water without using an enhanced distillation. In the literature, several entrainers have been studied for ethanol dehydration using heterogeneous azeotropic distillation: diisopropyl ether (DIPE), tert-amyl ethyl ether (TAME), methyl tert-butyl ether (MTBE), ETBE, cyclohexane, isooctane, hexane, pentane, isobutyl alcohol, toluene, etc. Benzene is discarded as carcinogenic and the entrainers with higher efficiency seems to be the gasoline additives. Many recent studies for alcohol dehydration agree with a heterogeneous azeotropic distillation process scheme that consists of two distillation columns and a decanter, where the first column works as prefractionator and for entrainer recovery. The aim of the nowadays proposed processes in the literature are the production of pure bioethanol that is later on mixed with gasoline. Stacey et al. (2016) analyzed a process that recovers the

bioethanol from the water and mixes it with the gasoline in the same process. This approach offers simple and practical improvements to existing bioethanol production processes. But the use of gasoline as liquid-liquid extractive agent for ethanol presents the disadvantage that the gasoline also recovers water which is a problem with the restrictive amount of water in gasoline. The risk associated with the use of inflammable compounds should be also considered (Palazzi et al., 2017).

Most of the best entrainers proposed for ethanol dehydration are also additives of gasoline that will be mixed later on with the gasoline together with the ethanol. It is not a problem that part of the entrainer remains mixed with the bioethanol. Greenhouse gases abatement costs are reduced if ethanol is produced at new facilities with fewer emissions or if petroleum output expansion causes greater emissions than the historical average (Johansson et al., 2020). Bioethanol dehydration represents around half of the energy share of its production (Aguilar-Sanchez et al., 2018). Additive mixing is a spontaneous process and combined with the ethanol dehydration process is expected to decrease its energy consumption. This study analyses this option to mix the gasoline additives with the bioethanol in the same process where the bioethanol is recovered from its aqueous solution.

2. Method

The simulations and the residue curve maps are calculated using the commercial simulation software Aspen Plus® v9. The thermodynamic model used is the NRTL, except for the ETBE where the UNIQUAC fits better the experimental liquid-liquid equilibrium data available in the Landolt-Börnstein Database (Springer Materials). Missing parameters are estimated by UNIFAC. The screening of entrainers is performed using the infinite/infinite analysis with the Distillation Sequence Efficiency (DSE) short cut method (Plesu et al., 2015). The shortcut method is implemented in Aspen based on SEP2 blocks. The rigorous simulations of selected entrainers are performed with RADFRAC blocks. The economic analysis is performed using the techno-economic tool available in Aspen Plus.

Several process schemes are evaluated in this paper: (1) single distillation column (DSE calculated as Eq(1)), (2) classical scheme of prefractionator + heterogeneous azeotropic distillation + entrainer recovery (3 columns, Figure 1b) (Eq(2)); (3) use of the prefractionator also for entrainer recovery (2 columns, Figure 1c) (Eq(3)); (4) entrainer collected with ethanol (2 columns, Figures 1d-e) (Eq(4) and Eq(5)), where w_i are the flow rates of process input, output and recycle streams and η_i is the Carnot efficiency of each distillation column calculated using the reboiler and condenser boiling point temperatures. The DSE method assumes that distillation columns are Carnot heat engines producing separation instead of work.

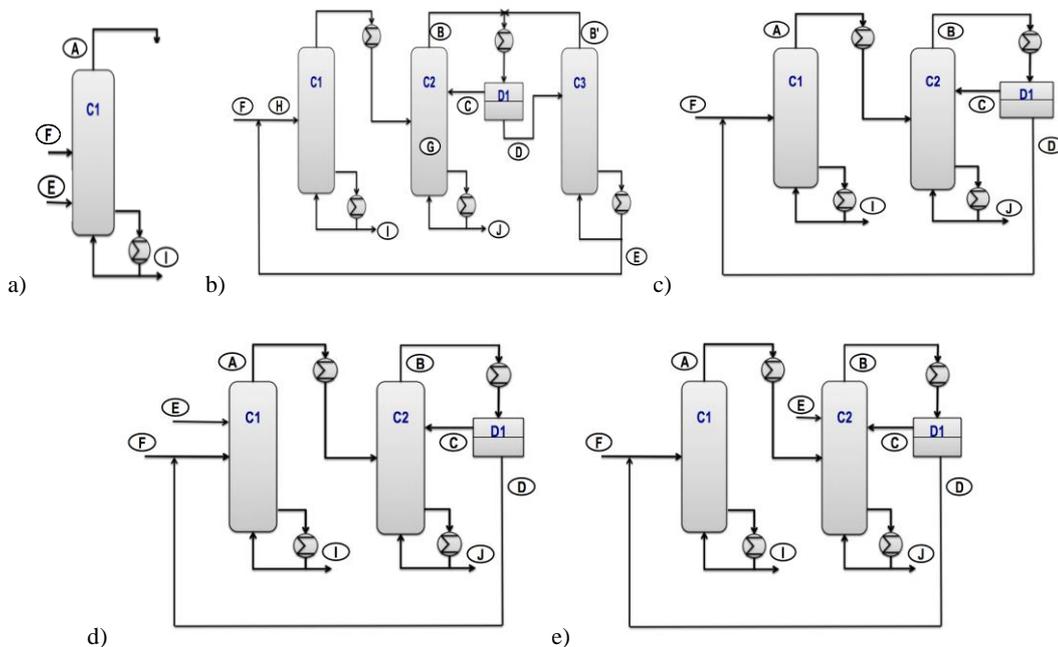


Figure 1: Process Schemes: (a) single distillation column, (b) without entrainer make-up and three columns, (c) without entrainer make-up and two columns, (d) with entrainer make-up at the first column and two columns, (e) with entrainer make-up at the second column and two columns.

$$DSE = \frac{w_I}{w_F} + \frac{w_A \eta_1}{w_F} \quad (1)$$

$$DSE = \frac{w_I}{w_F} + \frac{w_J \eta_1}{w_F} + \frac{w_E}{w_F} \cdot \left[\eta_1 \cdot \left(\frac{w_B \eta_2 + w_{B'}}{w_B + w_{B'}} \right) - 1 \right] \quad (2)$$

$$DSE = \frac{w_I}{w_F} + \frac{w_J \eta_1}{w_F} + \frac{(w_D \eta_1 \eta_2 - 1)}{w_F} \quad (3)$$

$$DSE = \frac{w_I}{w_F + w_E} + \frac{w_J \eta_1}{w_F + w_E} + \frac{(w_D \eta_1 \eta_2 - 1)}{w_F + w_E} \quad (4)$$

$$DSE = \frac{w_I}{w_F + w_E} + \frac{w_J \eta_1}{w_F + w_E} + \frac{(w_D \eta_1 \eta_2 - 1)}{w_F + w_E} + \frac{w_E}{w_F + w_E} \quad (5)$$

The rigorous simulations are performed assuming a feed stream calculation basis of 1,000 kmol/h with molar composition of 0.95 in water and 0.05 in ethanol at 1 bar. For gasoline additives, which are suitable to be blended with gasoline directly, a stream of entrainer (E) is added to the process scheme. This stream is calculated based on the gasoline E5 requirements (95 % gasoline and 5 % bioethanol, in molar fraction). Within this 5 % of ethanol, the maximum amount allowed for each entrainer (Schifter and López Salinas, 1998) is: MTBE: 10 % volume, ETBE: 17 % volume and TAME: 17 % volume (it depends on each country legislation). Using these values, the molar fraction and flowrate of each entrainer in the product is 0.489 and 48.0 kmol/h MTBE, 0.594 and 73.1 kmol/h TAME and 0.584 and 70.2 kmol/h ETBE. The distillation columns are optimized assuming an optimal reflux flow rate 1.3 times higher than its minimum (Bonet et al., 2007).

A fast to rigorous approach has been followed. First, the residue curve maps and Liquid-Liquid Equilibrium obtained for the ethanol dehydration with the several entrainers found in the literature are represented to visualize their thermodynamic behaviour. Next, processes efficiency assessments are performed using the DSE method. The best options selected (gasoline additives as entrainers) are rigorously simulated. The results of all the rigorous simulation are critically discussed and compared. A comparison between Li et al. (2015) simulation collecting pure ethanol and a novel proposed process is provided.

3. Results

3.1 Residue curve maps topologies

All the literature entrainers can be classified into three main residue curve map topologies, according to their similitude to: MTBE (Figure 2a), ETBE (Figure 2b) and TAME (Figure 2c) behaviour. The main difference between these three residue curve map topologies is the unstable node position. In MTBE case (Figure 2a), the unstable node, pale circle, has a binary composition in the immiscibility region ($x_{H_2O} = 0.1328$, $x_{MTBE} = 0.8672$). In ETBE case (Figure 2b), the unstable node is a binary composition in the miscibility region ($x_{EtOH} = 0.3886$, $x_{ETBE} = 0.6114$). Due to this fact, ETBE is a particular case where the ETBE/ethanol azeotrope can be separated from water in a single distillation column (Figure 1a). In TAME case (Figure 2c), the unstable node is a ternary composition in the immiscibility region ($x_{EtOH} = 0.2712$, $x_{H_2O} = 0.2752$, $x_{TAME} = 0.4536$). All compositions are expressed in mole fraction. All the entrainers proposed in the literature present a residue curve map topology similar to TAME: the ternary unstable node is in the immiscibility region.

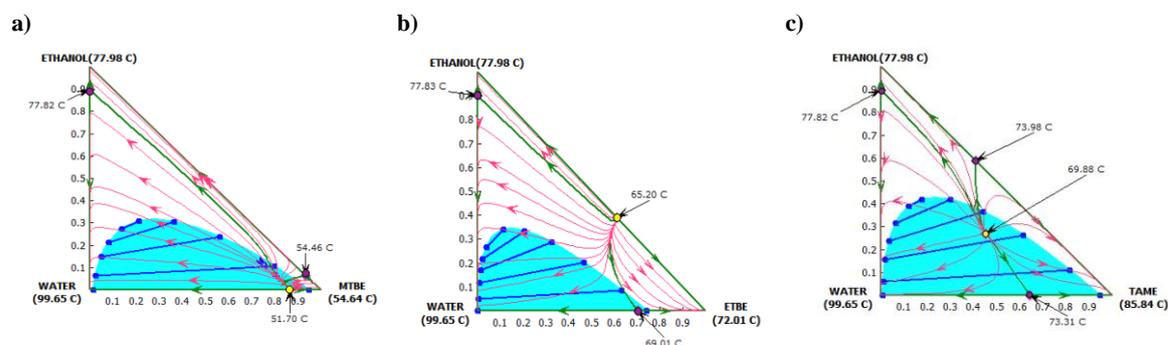


Figure 2. Residue curve maps topologies: a) MTBE; b) ETBE; c) TAME

3.2 Screening based on the Distillation Sequence Efficiency (DSE)

DSE values for the different entrainers and process schemes are provided in Table 1. As the DSE approaches to 1, the process efficiency is higher and so the values close to 1 are desired. DSE is higher in the process with two distillation columns (Figures 1c, d, e) than with three distillation columns (Figure 1b), the two columns process scheme is more efficient. DSE method is not able to indicate which the best entrainer is for the two distillation columns process (Figure 1c) and rigorous simulation would be required to rank them. High DSE values obtained for the entrainers that are gasoline additives. Their presence in the ethanol stream is not a problem because they can be mixed directly with gasoline. It is not necessary to obtain pure ethanol at the bottom of the second column (Figures 1d and 1e). The DSE value for ETBE entrainer case is then calculated using one distillation column due to the location of the azeotrope outside of the phase split envelope (Figure 2b). The DSE values indicate that feeding these entrainers in the second column (Figure 1e) is more efficient than in the first column (Figure 1d). According to these results, MTBE, ETBE and TAME are rigorously simulated in the following section for process scheme presented in Figure 1e.

Table 1: DSE results for the different entrainers and feasible process schemes

Entrainer	Figure 1a	Figure 1b	Figure 1c	Figure 1d	Figure 1e
Isooctane	-	0.88	0.95	-	-
Cyclohexane	-	0.89	0.95	-	-
Hexane	-	0.90	0.95	-	-
Methyl pentane	-	0.92	0.95	-	-
Toluene	-	0.92	0.95	-	-
Benzene	-	0.93	0.95	-	-
Cyclopentane	-	0.93	0.95	-	-
DIPE	-	0.95	0.95	-	-
Pentane	-	0.95	0.95	-	-
ETBE	0.01	-	-	-	-
MTBE	-	-	0.95	0.92	0.95
TAME	-	0.95	0.95	0.89	0.95

3.3 Rigorous simulations of the selected process

In this section, the process presented in Figure 1e is rigorously simulated using TAME and MTBE gasoline additives as entrainers. The rigorous simulation of the ETBE dehydration in a single column whose factibility has been presented in section 3.1 is also performed although the DSE analysis predicts a low efficiency. Rigorous simulation results (Table 2) are in agreement with DSE method results. ETBE is the entrainer that requires the highest reflux ratio and number of stages. Due to the high reflux, ETBE is the entrainer that generates the highest energy consumption and costs and is disregarded. Afterwards, the use of MTBE and TAME as entrainers determines the same reflux ratio in the first column. In the 2nd column, the reflux ratio is lower when using MTBE but TAME case requires fewer stages. However, TAME case requires 17 % more energy in reboiler and 34 % more energy in condenser than MTBE case. The capital costs are slightly lowered for TAME but its operating costs are a bit higher than MTBE. The costs associated to the TAME and MTBE processes are not different enough for a clear choice based only on economic criteria. From an environmental point of view, the MTBE process presents 15 % lower CO₂ emissions than TAME process as these emissions are directly related to the reboilers energy consumption. On the other hand, MTBE has been banned in many US states due to groundwater pollution problems produced by gas stations leakages (Flannagan et al., 2017). Leakage risk is avoided in gas stations using double wall storage tanks with leak detection.

Table 2: Results of the rigorous simulation

Parameter	Units	MTBE	TAME	ETBE
Number stage C1		23	18	60
Number stage C2		30	18	-
Reflux ratio C1		4.05	4.05	28
Reflux ratio C2		4.15	5.15	-
Total heat duty (reboiler)	kW	5,821	6,826	31,943
Total heat duty (condenser)	kW	5,629	8,653	32,114
Total capital cost*	USD	5,611,580	5,494,150	7,692,500
Total operating cost*	USD/y	3,224,210	3,525,140	11,559,500

The amount of energy saved collecting a mixture of ethanol/MTBE as proposed in this study instead of pure ethanol as proposed in the existing literature is of 27 % for the reboilers duty and close to 14 % for the condensers duty. 27 % of CO₂ emissions are avoided. Nowadays, TAME is the gasoline additive most widely used and the following section provides the rigorous simulation for this compound in detail.

3.4 TAME case study

The simulation results for the TAME case study are presented in this section in more detail; the corresponding process scheme is presented in Fig 1e (Table 3). For the distillation column (C1) the optimum feed stage is situated in the 14th stage numbered from the top while the optimum stage number and optimum reflux ratio are 18 and 4.05. The C1 bottom flow rate (stream I) is 950 kmol/h (Table 3). For the second distillation column (C2), there are three feed stream. The first one is situated in 12th stage, which is the top stream from C1. The second one is situated in 3rd stage, which is the entrainer make-up. The third one is situated in 1st stage, which is the recirculated stream from the decanter (D1). The optimum stage number is 18 and the optimum reflux ratio is 5.15. The product collected at the bottom of C2 is a mixture ethanol/TAME with the desired molar composition according to gasoline formulation. The column profiles are in Figure 3. Stream I is water almost free of ethanol and entrainer. The stream J is a mixture ethanol/TAME close to the maximum amount allowed to blend directly with gasoline. The water content in stream J is lower than the maximum amount allowed to blend with gasoline directly, 0.3 % in mass (Table 3).

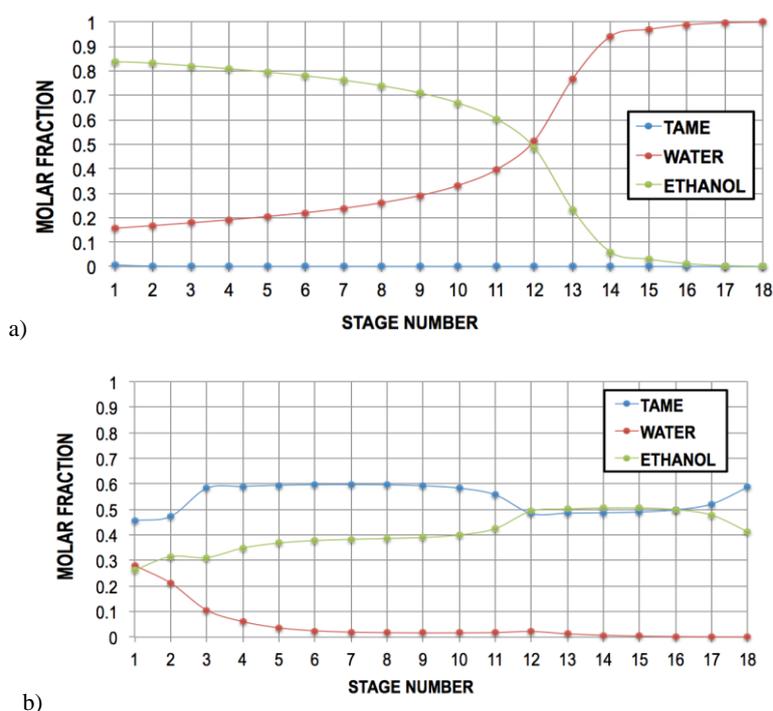


Figure 3. TAME Column profile of the (a) first and (b) second distillation column. Stages numbered from top to bottoms.

Table 3: TAME General streams results (Figure 1e)

Parameter	Units	A	B	C	D	E	F	I	J
Temperature	°C	77.7	68.9	70.6	70.6	85.8	89.9	99.3	74.4
Flow rate	kmol/h	60.98	61.42	50.43	11.03	73.12	1000	950	123.07
TAME	mol frac.	0.005	0.457	0.535	0.026	1.000	0.000	0.000	0.587
water	mol frac.	0.157	0.280	0.153	0.782	0.000	0.950	0.999	0.000
ethanol	mol frac.	0.839	0.263	0.312	0.192	0.000	0.050	0.001	0.412

4. Conclusions

The most common entrainers used for ethanol dehydration using heterogeneous azeotropic distillation are: DIPE, TAME, MTBE, ETBE, cyclohexane, isooctane and hexane, i.e. gasoline additives and hydrocarbons. The DSE method is used for screening, indicating that gasoline additives are a good choice as entrainers. The use of the prefractionator also for entrainer recovery (2 columns) is more efficient than a classical scheme of prefractionator + heterogeneous azeotropic distillation + entrainer recovery (3 columns). The use of gasoline additives as entrainers allows collecting a mixture of ethanol and entrainer suitable to be blend with gasoline, in this case TAME and MTBE are more advantageous than ETBE although this one could be collected in a single distillation column. Comparing the results of using MTBE as entrainer to collect pure ethanol or collecting a mixture of ethanol and MTBE suitable for gasoline blending shows that this second option provides great energy savings in the distillation operation, i.e. 27 %. A novel process scheme using two distillation columns with the MTBE or TAME feed to the second distillation column to collect a mixture of ethanol/entrainer useful for gasoline blending is then proposed instead of collecting pure ethanol. It is stated that collecting a mixture of ethanol with a gasoline additive decreases the energy consumption of ethanol dehydration. The CO₂ emissions are directly proportional to the energy consumed in the distillation column reboilers, which the novel process contributes to reduce the greenhouse gases emissions of the fuel bioethanol production process.

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References

- Aguilar-Sánchez P., Navarro-Pineda F.S., Sacramento-Rivero J.C., Barahona-Pérez L.F., 2018, Life-cycle assessment of bioethanol production from sweet sorghum stalks cultivated in the state of Yucatan, Mexico, *Clean Technologies and Environmental Policy*, 20(7), 1685-1696.
- Bonet J., Galan M.-I., Costa J., Meyer X.M., Meyer M., 2007, Multicomponent rectification: representation of number of stages as function of reflux ratio, *Proceedings of European Congress of Chemical Engineering (ECCE-6) Copenhagen*, 16-20 September.
- Cardona C.A., Sánchez Ó.J., 2007, Fuel ethanol production: process design trends and integration opportunities, *Bioresource Technology*, 98, 2415–2457.
- European Committee for Standardisation, Automotive Fuels. Ethanol as a Blending Component for Petrol. Requirements and Test Methods, *European Standard EN 15376*, 2011.
- Flanagan S.M., Levitt J.P., Ayotte J.D., 2017, Trends in Methyl tert-Butyl Ether Concentrations in Private Wells in Southeast New Hampshire: 2005 to 2015, *Environmental Science and Technology*, 51(3), 1168-1175.
- Johansson R., Meyer S., Whistance J., Thompson W., Debnath D., 2020, Greenhouse gas emission reduction and cost from the United States biofuels mandate, *Renewable and Sustainable Energy Reviews*, 119, 109513.
- Kiss A.A., Suszwalak D.J.P.C., 2012, Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns, *Separation and Purification Technology*, 86, 70-78.
- Li J., You C., Lyu Z., Zhang C., Chen L., Qi Z., 2015, Fuel-based ethanol dehydration process directly extracted by gasoline additive, *Separation and Purification Technology*, 149, 9-15.
- Li Y., Liu G., 2018, Study on coupling separation process of ETBE and absolute ethanol, *Chemical Engineering Transactions*, 2018, 70, 427-432
- Palazzi E., Caviglione C., Reverberi A.P., Fabiano B., 2017, A short-cut analytical model of hydrocarbon pool fire of different geometries, with enhanced view factor evaluation, *Process Safety and Environmental Protection*, 110, 89-101.
- Plesu V., Bonet Ruiz A.E., Bonet J., Llorens J., Iancu P., 2015, Shortcut assesment of alternative distillation sequence schemes for process intensification, *Computer & Chemical Engineering*, 83, 58-71.
- Rezania S., Oryani B., Cho J., Talaiekhosani A., Sabbagh F., Hashemi B., Rupani P.F., Mohammadi A.A., 2020, Different pretreatment technologies of lignocellulosic biomass for bioethanol production: An overview, *Energy*, 199, 117457
- Roukas T., Kotzekidou P., 2020, Rotary biofilm reactor: A new tool for long-term bioethanol production from non-sterilized beet molasses by *Saccharomyces cerevisiae* in repeated-batch fermentation, *Journal of Cleaner Production*, 257, 120519.
- Stacey N.T., Hadjithodorou A., Glasser D., 2016, Gasoline Preblending for Energy-Efficient Bioethanol Recovery, *Energy and Fuels*, 30(10), 8286-8291.