



# The Efficiency of Refrigeration Capacity Regulation in the Ambient Air Conditioning Systems

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**Abstract.** The operation of the ambient air conditioning systems (ACS) is characterized by considerable fluctuations of the heat load in response to the current climatic conditions. It needs the analyses of the efficiency of the application of compressors with frequency converters for refrigeration capacity regulation in actual climatic conditions. A new method and approach to analyzing the effectiveness of ACS cooling capacity adjusting by using the compressor with changing the rotational speed of the motor as an example have been developed, according to which the overall range of changeable heat loads is divided into two zones: the zone of ambient air processing with considerable fluctuations of the current heat load, that requires effective refrigeration capacity regulation by the compressor with frequency converters (from 100% rated refrigeration capacity down to about 50%) and not an adjustable zone of reduced refrigeration capacity below 50% rated refrigeration capacity of the compressor. The magnitudes of threshold refrigeration capacity between both zones are chosen according to the rational value of installed (design) refrigeration capacity on the ACS, required for cooling the ambient air to a target temperature that ensures the maximum annual refrigeration capacity production in actual current climatic conditions. The proposed method and approach to the analysis of the efficiency of the refrigeration capacity regulation of the ACS compressor by distributing the overall range of changes in current heat loads allows increasing the efficiency of utilizing the installed refrigeration capacity in prevailing climatic conditions.

**Keywords:** Ambient air processing · Stable heat load · Changeable heat load · Threshold refrigeration capacity · Refrigeration capacity distribution

## 1 Introduction

Significant fluctuations of the heat load characterize the operation of the ambient air conditioning systems (ACS) under the current ambient air temperature  $t_{amb}$  and relative humidity  $\varphi_{amb}$  [1, 2]. At the same time, the operation of closed type ACS (processing of indoor air) is characterized by relatively insignificant fluctuations in the heat load on the air coolers (AC), corresponding to changes in the room air temperature within a

narrow range (about 5 °C). For such closed type ACS it is advantageous to use compressors with frequency converters that provide refrigeration capacity regulation from nominal (rated) to 50% of nominal and lower.

The study aims to develop an approach to the analysis of the efficiency of regulating the refrigeration capacity of an ACS compressor with a frequency converter for actual climatic conditions.

## 2 Literature Review

In a number of investigations, the air conditioning is considered as one of the technologies for combined cooling, heating, and power (CCHP) [3, 4]. Some of the technical innovations and methodological approaches in waste heat recovery might be applied for traditional refrigeration technologies in air conditioning, in particular, the evaporative cooling [5], two-stage air-cooling, as well as methods to choose rational design value of refrigeration capacity to match current cooling demand [6–8].

Numerous researchers have studied the energy efficiency of the VRF system [9, 10] and proposed some practical recommendations [11, 12]. The simulation results in work [13] show that the VRF systems would save around 15–42% and 18–33% for HVAC site and source energy uses compared to the rooftop unite variable air volume systems (RTU-VAV) systems. The author [14] proposes the method of calculating the thermal load of a building. The VRF systems operate with high part-load efficiency [15, 16], which results in top daily and seasonal energy efficiency. Hence, as ACS typically spend most of their operating hours  $\tau$  in the range of 40% to 80% of maximum capacity [17]. Results [18] show that ACS have great potential for energy saving, and the adjustability of VRF ACS is better than that of a centralized air conditioning system. The authors [19] study analyzes the cooling load rules of a typical room comparatively under the intermittent and continuous running of ACS.

A combination of the HVAC system with RTU used as the outdoor air processing (OAP) system in the VRF and control strategies to enhance its energy performance and thermal comfort was proposed [10, 20]. The VRF system with energy recovery ventilation (ERV) [21] and a dedicated outdoor air system (DOAS) was introduced [22]. The evaluation of indoor thermal environments and energy consumption of the VRF system [23, 24] with a heat pump desiccant (HPD) was conducted [25].

The HVAC system that processed outdoor air loads by supplying refrigerant from the outdoor unit performed simultaneously as an outdoor unit in the VRF system in contrast with the OAP, which had compressors [26]. In the VRF-OAP system, the multiple indoor units and the OAP were simultaneously connected to an outdoor unit.

The authors [27] developed a control algorithm of the supply air temperature (threshold temperature) in the outdoor air processing (OAP). A higher energy reduction compared with the conventional operation without refrigerant flow regulation, revealed when the outdoor air temperature was closer to the indoor temperature setpoint, was quite evident due to superlative applying the variable speed compressor in part-load modes. The authors [28] on the base of field test results revealed that the actual OAP capacity should be less than 30% of the design outdoor unit capacity to prevent a lack of indoor unit cooling capacities.

### 3 Research Methodology

In the general case, an overall heat load of any ACS comprises the unstable heat load zone, corresponding to ambient (outdoor) air processing with considerable heat load fluctuations in response to actual climatic conditions, and a comparatively stable heat load zone for subsequent air cooling (subcooling) to a target temperature.

In modern VRF systems, the load modulation is performed by varying refrigerant feed to air coolers. The COP and the specific (per unit of refrigerant mass flow) generated refrigeration capacity are stabilized due to a change in the rotational speed of the piston compressor while reducing the heat load to 50% of the nominal.

Authors developed a methodological approach to the analysis of the efficiency of regulation of the cooling capacity of ACS in actual climatic conditions, according to which the overall range of changes in current heat loads is divided into two zones: a zone of effective regulation of the refrigeration capacity without energy loss and a zone of the reduced not adjustable (unregulated) refrigeration capacity.

For the convenience of calculation for other refrigeration capacities of ACS the heat loads are represented in relative (specific) values per unit air mass flow ( $G_a = 1 \text{ kg/s}$ ) – as specific heat load, or refrigeration capacity of a refrigerating machine (RM),

$$q_0 = Q_0/G_a, \text{kJ/kg}, \tag{1}$$

where  $Q_0$  is the total heat load (refrigeration capacity) for airflow  $G_a$ .

The rational value  $q_{0.rat}$  of specific refrigeration capacity  $q_0$  on the AC, required for cooling the ambient air to a target temperature of 10 °C, ensures the maximum specific annual refrigeration capacity production  $\sum (q_0 \cdot \tau)$  taking into account the actual current climatic conditions [29]. The specific cooling capacity is calculated as follows:

$$q_0 = \xi \cdot c_{ma} \cdot (t_{amb} - t_{a2}), \text{kJ/kg}, \tag{2}$$

where:  $\xi$  – coefficient of water vapor condensation heat, calculated as a ratio of the overall heat removed from the air being cooled, including the latent heat of water vapor condensed from the ambient air to the sensible heat transferred;  $c_a$  – humid air specific heat. The specific annual refrigeration capacity production

$$\sum (q_0 \cdot \tau) = \sum (\xi \cdot c_a \cdot (t_{amb} - t_{a2}) \cdot \tau). \tag{3}$$

The specific refrigeration capacity consumption in the zone of its frequency regulation  $q_{0.10/2reg} > 0$  (positive values in the area of adjustable refrigeration capacity from 100 to 50% – above threshold value  $q_{0.10rat}/2$ ) defined as  $q_{0/2reg} > 0 = q_0 - q_{0.rat}/2 \geq 0$ , as well as below the range of its frequency regulation  $q_{0.10/2reg} < 0$  (positive values in the unregulated range of refrigeration capacity below 50% – below  $q_{0.10rat}/2$ ):  $q_{0/2reg} < 0 = q_{0rat}/2 - q_0 \geq 0$ . The values of the unused excess of the installed refrigeration capacity:  $q_{0.10rat}/2 - q_{0.10/2reg} > 0$  in the zone of its frequency regulation (above  $q_{0.10rat}/2$ ), its excess:  $q_{0.10rat}/2 - q_{0.10/2reg} < 0$  outside the range of its control (below

$q_{0.10rat}/2$ ), the total expenditures of increasing consumption  $\sum (q_{0.10/2reg > 0} \cdot \tau) = \sum [(q_{0.10} - q_{0.10rat}/2) \cdot \tau] \geq 0$  and excess of refrigeration capacity  $\sum [(q_{0.10rat}/2 - q_{0.10/2reg > 0}) \cdot \tau] = q_{0.10} - q_{0.10rat}/2 \geq 0$  in the zone of its regulation (above  $q_{0.10rat}/2$ ) and consumption  $\sum (q_{0.10/2reg < 0} \cdot \tau) = \sum [(q_{0.10rat}/2 - q_{0.10}) \cdot \tau] \geq 0$  and excess of installed refrigeration capacity  $\sum [(q_{0.10rat}/2 - q_{0.10/2reg < 0}) \cdot \tau] = \sum [(q_{0.10} - q_{0.10rat}/2) \cdot \tau] \geq 0$  below the range of its regulation (lower  $q_{0.10rat}/2$ ).

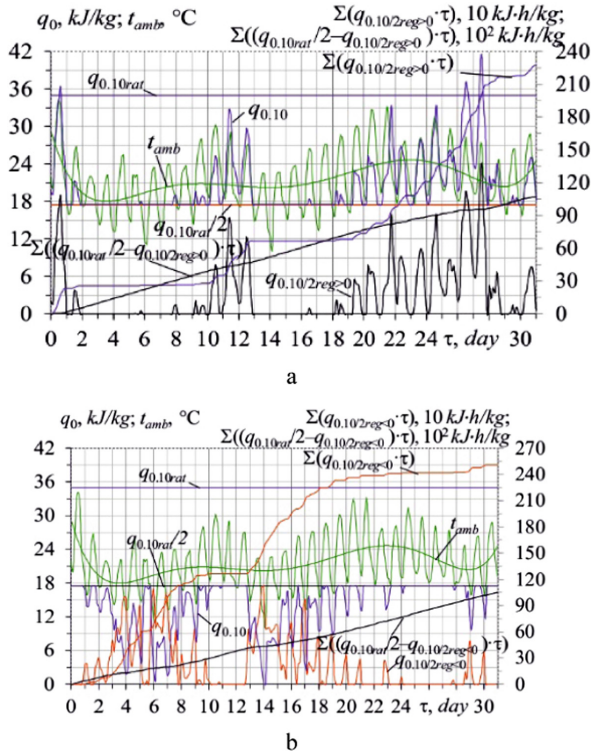
## 4 Results

For the climatic conditions of the south of Ukraine, when the air is cooled to  $t_{a2} = 10$  °C, the maximum specific annual refrigeration capacity production  $\sum (q_0 \cdot \tau)$  takes place at the specific refrigeration capacity  $q_0 \approx 34$  kJ/kg as rational  $q_{0, rat}$  [29]. Current values of  $t_{amb}$ , specific heat loads at the ACS air cooler (AC)  $q_{0.10}$ , consumption of the specific refrigeration capacity in the zone of its frequency regulation  $q_{0.10/2reg > 0} = q_{0.10} - q_{0.10rat}/2 \geq 0$  (positive values in the area of adjustable refrigeration capacity from 100 to 50% – above threshold value  $q_{0.10rat}/2$  in Fig. 1a and below the range of its frequency regulation  $q_{0.10/2reg < 0} = q_{0.10rat}/2 - q_{0.10} \geq 0$  (positive values in the unregulated range of refrigeration capacity below 50% – below  $q_{0.10rat}/2$  in Fig. 1b) for climatic conditions (Voznesensk, Mykolaiv region, 2015) are shown in Fig. 1.

As Fig. 1 shows, the share of cold production at 50% frequency regulation of the refrigeration capacity is  $\sum (q_{0.10/2reg > 0} \cdot \tau) / (\sum (q_{0.10/2reg > 0} \cdot \tau) + \sum (q_{0.10/2reg < 0} \cdot \tau)) \approx 0,47$ , i.e. about 47% of the total monthly amount of cold spent for cooling the air in the range of variation of the current heat load  $q_{0.10}$  from 0 to  $q_{0.10rat} = 34$  kJ/kg. However, with respect to the unused monthly excess of the installed cooling capacity over the expendable for cooling the air  $\sum [(q_{0.10rat}/2 - q_{0.10/2reg > 0}) \cdot \tau] = q_{0.10} - q_{0.10rat}/2 \geq 0$  in the region of 50% of its frequency regulation, the share of refrigeration capacity monthly production is  $2200/(2200 + 10500) \approx 0,17$  (Fig. 1a, i.e., about 17%, and almost half as much  $(2200/[2(2200 + 10500)]) \approx 0,087$ ) in the entire range of changes in the current heat load  $q_{0.10}$  from 0 to  $q_{0.10rat} = 34$  kJ/kg for the July.

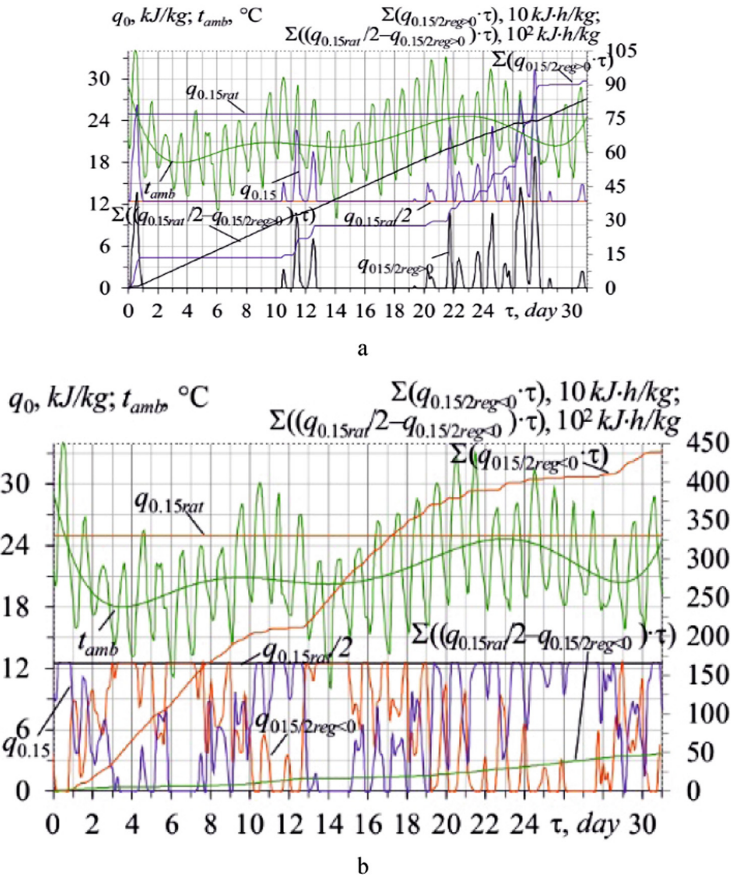
This indicates, firstly, the presence of significant reserves to increase the efficiency of ACS by using the excess of the installed refrigeration capacity over that consumed for cooling air, in particular, by accumulating it for subsequent consumption, which provides a significant reduction in the installed refrigeration capacity, and secondly, the possibility to use other methods of regulating the refrigeration capacity in addition to changing the speed of the compressor motor, for example, by turning off the cylinders or the compressor itself in the case of several compressors, etc.

If ACS operates in June or August, the efficiency of applying the refrigeration capacity control by changing the rotational speed of the compressor electric motor will be even lower, and taking into account 3–5 times higher cost of compressors with frequency converters, their application for ACS becomes problematic.



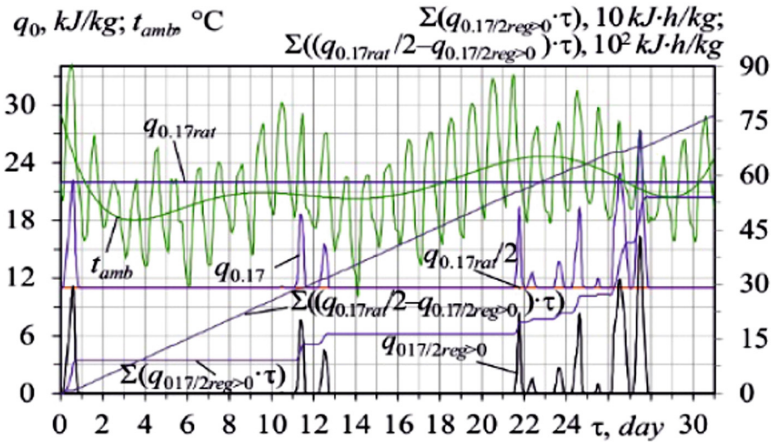
**Fig. 1.** Current values of  $t_{amb}$ , refrigeration capacity  $q_{0,10}$ , consumption  $q_{0,10/2reg > 0}$  and unused excess  $(q_{0,10rat}/2 - q_{0,10/2reg > 0})$ , total monthly consumption  $\Sigma(q_{0,10/2reg > 0} \cdot \tau)$  and excess  $\Sigma[(q_{0,10rat}/2 - q_{0,10/2reg > 0}) \cdot \tau]$  within frequency regulation (a), values of  $q_{0,10/2reg < 0}$  and  $(q_{0,10rat}/2 - q_{0,10/2reg < 0})$ ,  $\Sigma(q_{0,10/2reg < 0} \cdot \tau)$  and  $\Sigma[(q_{0,10rat}/2 - q_{0,10/2reg < 0}) \cdot \tau]$  below regulation (b):  $q_{0,10/2reg > 0} = q_{0,10} - q_{0,10rat}/2 \geq 0$  (adjustable range);  $q_{0,10/2reg < 0} = q_{0,10rat}/2 - q_{0,10} \geq 0$  (unregulated range); threshold value  $q_{0,10rat}/2 \approx 17$  kJ/kg.

When the ambient air is being cooled from  $t_{amb}$  to the higher temperatures  $t_{a2} = 15, 17$  and  $20$   $^{\circ}\text{C}$ , as the cooling temperature  $t_{a2}$  rises a significant proportion of the unstable heat load is replaced from its adjustable range ( $q_{0/2reg > 0} = q_0 - q_{0,10rat}/2 \geq 0$ ), which falls on the  $q_0 \geq q_{0,10rat}/2$ , into the range of unregulated heat load  $q_0 \leq q_{0,10rat}/2$  (Fig. 2, 3 and 4).

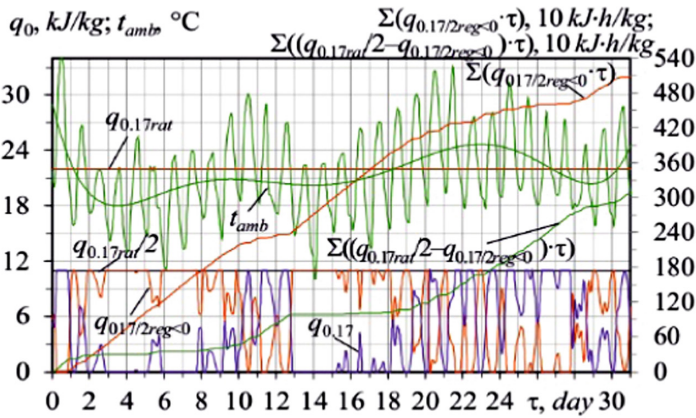


**Fig. 2.** Current values of  $t_{amb}$ , specific refrigeration capacity of ACS  $q_{0.15}$ , consumption of refrigeration capacity  $q_{0.15/2reg > 0}$  and unused excess of installed refrigeration capacity ( $q_{0.15rat}/2 - q_{0.15/2reg > 0}$ ), the total monthly consumption  $\Sigma(q_{0.15/2reg > 0} \cdot \tau)$  and excess  $\Sigma[(q_{0.15rat}/2 - q_{0.15/2reg > 0}) \cdot \tau]$  of refrigeration capacity within frequency regulation (a), values of  $q_{0.15/2reg < 0}$  and  $(q_{0.15rat}/2 - q_{0.15/2reg < 0})$ ,  $\Sigma(q_{0.15/2reg < 0} \cdot \tau)$  and  $\Sigma[(q_{0.15rat}/2 - q_{0.15/2reg < 0}) \cdot \tau]$  below the range of its regulation (b) when cooling the ambient air from  $t_{amb}$  to  $t_{a2} = 15^{\circ}\text{C}$ :  $q_{0.15/2reg > 0} = q_{0.15} - q_{0.15rat}/2 \geq 0$  (adjustable range);  $q_{0.15/2reg < 0} = q_{0.15rat}/2 - q_{0.15} \geq 0$  (unregulated range); threshold value  $q_{0.15rat}/2 \approx 12$  kJ/kg.

As Fig. 2 shows, the share of the refrigeration capacity monthly production at 50% frequency regulation of refrigeration capacity is:  $\Sigma(q_{0.15/2reg > 0} \cdot \tau) / (\Sigma(q_{0.15/2reg > 0} \cdot \tau) + \Sigma(q_{0.15/2reg < 0} \cdot \tau)) \approx 0,17$ , i.e., about 17% of the total monthly amount of the refrigeration capacity expended for cooling the air in the range of variation of the current heat load  $q_{0.15}$  from 0 to  $q_{0.15rat} = 25$  kJ/kg.



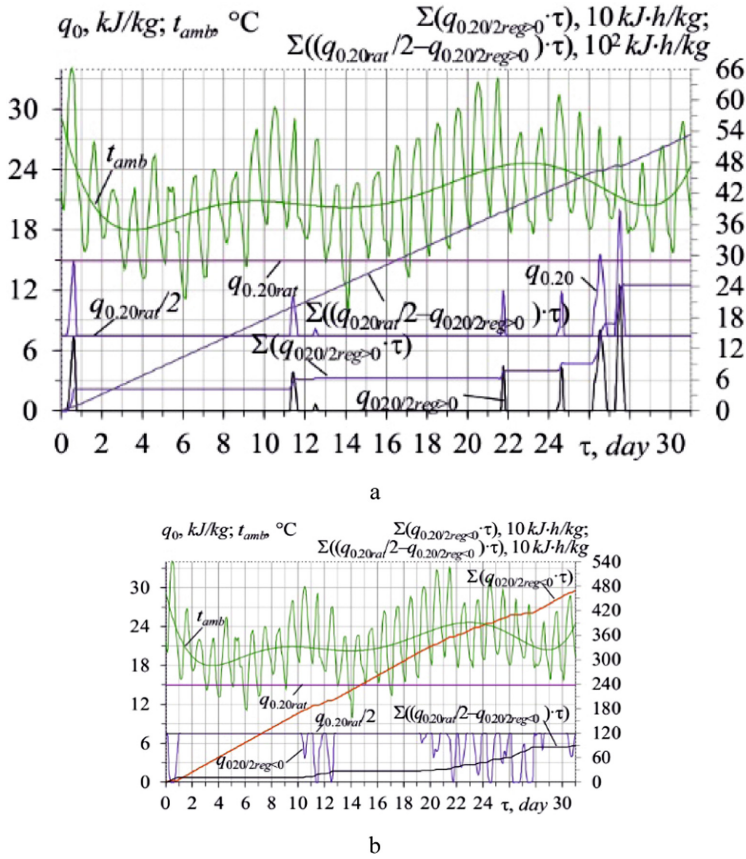
a



b

**Fig. 3.** Current values of  $t_{amb}$ , specific refrigeration capacity  $q_{0.15}$ , consumption  $q_{0.17/2reg > 0}$  and unused excess of installed refrigeration capacity  $(q_{0.17rat}/2 - q_{0.17/2reg > 0})$ , the total monthly consumption  $\sum (q_{0.20/2reg > 0} \cdot \tau)$  and excess  $\sum [(q_{0.17rat}/2 - q_{0.17/2reg > 0}) \cdot \tau]$  of refrigeration capacity within frequency regulation (a), values of  $q_{0.17/2reg < 0}$  and  $(q_{0.17rat}/2 - q_{0.17/2reg < 0})$ ,  $\sum (q_{0.17/2reg < 0} \cdot \tau)$  and  $\sum [(q_{0.17rat}/2 - q_{0.17/2reg < 0}) \cdot \tau]$  below the range of its regulation (b) when cooling the ambient air from  $t_{amb}$  to  $t_{a2} = 17 \text{ }^\circ\text{C}$ :  $q_{0.17/2reg > 0} = q_{0.17} - q_{0.17rat}/2 \geq 0$  (adjustable range);  $q_{0.17/2reg < 0} = q_{0.17rat}/2 - q_{0.17} \geq 0$  (unregulated range); threshold value  $q_{0.17rat}/2 \approx 11 \text{ kJ/kg}$ .

The share of the refrigeration capacity monthly production at 50% frequency regulation of refrigeration capacity is:  $\sum (q_{0.17/2reg > 0} \cdot \tau) / (\sum (q_{0.17/2reg > 0} \cdot \tau) + \sum (q_{0.17/2reg < 0} \cdot \tau)) \approx 0.093$ , i.e. about 9.3% of the total monthly amount of the refrigeration capacity expended for cooling the air in the range of variation of  $q_{0.17}$  from 0 to  $q_{0.17rat} = 22 \text{ kJ/kg}$  (Fig. 3).



**Fig. 4.** Current values of  $t_{amb}$ , consumption of specific refrigeration capacity  $q_{0.20/2reg} > 0$  and unrealized excess of installed refrigeration capacity ( $q_{0.20rat}/2 - q_{0.20/2reg} > 0$ ), the total monthly consumption  $\sum (q_{0.20/2reg} > 0 \cdot \tau)$  and excess  $\sum [(q_{0.20rat}/2 - q_{0.20/2reg} > 0) \cdot \tau]$  of refrigeration capacity within frequency regulation (a), values of  $q_{0.20/2reg} < 0$  and ( $q_{0.20rat}/2 - q_{0.20/2reg} < 0$ ),  $\sum (q_{0.20/2reg} < 0 \cdot \tau)$  and  $\sum [(q_{0.20rat}/2 - q_{0.20/2reg} < 0) \cdot \tau]$  below the range of its regulation (b) when cooling the ambient air from  $t_{amb}$  to  $t_{a2} = 20^{\circ}\text{C}$ :  $q_{0.20/2reg} > 0 = q_{0.20} - q_{0.20rat}/2 \geq 0$  (adjustable range);  $q_{0.20/2reg} < 0 = q_{0.20rat}/2 - q_{0.20} \geq 0$  (unregulated range); threshold value  $q_{0.20rat}/2 \approx 7.5 \text{ kJ}/\text{kg}$ .

As Fig. 4 shows, the share of the refrigeration capacity monthly production at 50% frequency regulation of the refrigeration capacity is  $\sum (q_{0.20/2reg} > 0 \cdot \tau) / (\sum (q_{0.20/2reg} > 0 \cdot \tau) + \sum (q_{0.20/2reg} < 0 \cdot \tau)) \approx 0.05$ , i.e., about 5% of the total amount of the refrigeration capacity monthly spent for cooling the air in the range of changes in the current heat load  $q_{0.20}$  from 0 to  $q_{0.20rat} = 15 \text{ kJ}/\text{kg}$ , which indicates an extremely low efficiency of regulation of ACS refrigeration capacity by the speed of rotation of the piston electric motor compressor and the need for other control methods.



## 5 Conclusions

A method and approach to the analysis of the efficiency of regulation of the refrigeration capacity of ACS in actual climatic conditions is proposed, according to which the entire range of changes in current heat loads is divided in two zones: a zone of ambient air processing with considerable fluctuations of the current heat load, that requires effective refrigeration capacity regulation by compressor with frequency converters (from 100% rated refrigeration capacity down to about 50%) and a not adjustable zone of the reduced refrigeration capacity below 50% rated refrigeration capacity of compressor. The magnitudes of threshold refrigeration capacity between both zones are chosen according to the rational value of the installed refrigeration capacity on the ACS, required for cooling the ambient air to a target temperature that ensures the maximum annual refrigeration capacity production in actual climatic conditions.

It is shown that for the summer month, the proportion of the refrigeration capacity monthly consumed for cooling the ambient air to the target temperature with a 50% frequency control of the refrigeration capacity is about 10% of its total amount that could be monthly produced at rated load. This fact indicates a low efficiency of regulating the refrigeration capacity of ACS by changing the rotation speed of the reciprocating compressor electric motor and the need for other control methods.

The proposed method and approach to the analysis of the efficiency of the refrigeration capacity regulation of the ACS compressor by distributing the overall range of changes in current heat loads allows revealing the reserves for increasing the efficiency of utilizing the installed refrigeration capacity in prevailing climatic conditions.

## References

1. Marque, R.P., Hacon, D., Tessarollo, A., Parise, J.A.R.: Thermodynamic analysis of trigeneration systems taking into account refrigeration, heating and electricity load demands. *Energy Build.* **42**, 2323–2330 (2010)
2. Ortiga, J., Carles, B.J., Alberto, C.: Operational optimization of a complex trigeneration system connected to a district heating and cooling network. *Appl. Therm. Eng.* **50**, 1536–1542 (2013)
3. Radchenko, M., Radchenko, R., Ostapenko, O., Zubarev, A., Hrych, A.: Enhancing the utilization of gas engine module exhaust heat by two-stage chillers for combined electricity, heat and refrigeration. In: 5th International Conference on Systems and Informatics, ICSAI 2018, Jiangsu, Nanjing, China, pp. 227–231 (2018)
4. Sugiarta, N., Tassou, S.A., Chaer, I., Marriott, D.: Trigeneration in food retail: an energetic, economic and environmental evaluation for a supermarket application. *Appl. Therm. Eng.* **29**, 2624–2632 (2009)
5. Eidan, A.A., Alwan, K.J.: Enhancement of the performance characteristics for air-conditioning system by using direct evaporative cooling in hot climates. *Energy Procedia* **142**, 3998–4003 (2017)
6. Radchenko, A., Radchenko, M., Trushliakov, E., Kantor, S., Tkachenko, V.: Statistical method to define rational heat loads on railway air conditioning system for changeable climatic conditions. In: 5th International Conference on Systems and Informatics, ICSAI 2018, Jiangsu, Nanjing, China, pp. 1308–1312 (2018)

7. Radchenko, R., Radchenko, A., Serbin, S., Kantor, S., Portnoi, B.: Gas turbine unite inlet air cooling by using an excessive refrigeration capacity of absorption-ejector chiller in booster air cooler. In: HTRSE-2018, E3S Web of Conferences, vol. 70, p. 6 (2018)
8. Trushliakov, E., Radchenko, M., Radchenko, A., Kantor, S., Zongming, Y.: Statistical approach to improve the efficiency of air conditioning system performance in changeable climatic conditions. In: 5th International Conference on Systems and Informatics, ICSAI 2018, Jiangsu, Nanjing, China, pp. 1303–1307 (2018)
9. Alahmer, A., Alsaqoor, S.: Simulation and optimization of multi-split variable refrigerant flow systems. *Ain Shams Eng. J.* **9**, 1705–1715 (2017)
10. Chua, K.J., Chou, S.K., Yang, W.M., Yan, J.: Achieving better energy-efficient air conditioning – a review of technologies and strategies. *Appl. Energy* **104**, 87–104 (2013)
11. Yun, G.Y., Choi, J., Kim, J.T.: Energy performance of direct expansion air handling unit in office buildings. *Energy Build.* **77**, 425–431 (2014)
12. Yun, G.Y., Lee, J.H., Kim, H.J.: Development and application of the load responsive control of the evaporating temperature in a VRF system for cooling energy savings. *Energy Build.* **116**, 638–645 (2016)
13. Kim, D., Cox, S.J., Cho, H., Im, P.: Evaluation of energy savings potential of variable refrigerant flow (VRF) from variable air volume (VAV) in the U.S. climate locations. *Energy Rep.* **3**, 85–93 (2017)
14. Sait, H.H.: Estimated thermal load and selecting of suitable air-conditioning systems for a three story educational building. *Procedia Comput. Sci.* **19**, 636–645 (2013)
15. Ilie, A., Dumitrescu, R., Girip, A., Cublesan, V.: Study on technical and economical solutions for improving air-conditioning efficiency in building sector. *Energy Procedia* **112**, 537–544 (2017)
16. Li, Y., Wu, J., Shiochi, S.: Modeling and energy simulation of the variable refrigerant flow air conditioning system with water-cooled condenser under cooling conditions. *Energy Build.* **41**, 949–957 (2009)
17. Enteria, N., Yamaguchi, H., Miyata, M., Sawachi, T., Kuwasawa, Y.: Performance evaluation of the variable refrigerant flow (VRF) air-conditioning system subjected to partial and unbalanced thermal loadings. *J. Therm. Sci. Technol.* **11**(1), 1–11 (2016)
18. Liu, C., Zhao, T., Zhang, J.: Operational electricity consumption analyze of VRF air conditioning system and centralized air conditioning system based on building energy monitoring and management system. *Procedia Eng.* **121**, 1856–1863 (2015)
19. Zhang, L., Wang, Y., Meng, X.: Qualitative analysis of the cooling load in the typical room under continuous and intermittent runnings of air-conditioning. *Procedia Eng.* **205**, 405–409 (2017)
20. Zhu, Y., Jin, X., Du, Z., Fang, X., Fan, B.: Control and energy simulation of variable refrigerant flow air conditioning system combined with outdoor air processing unit. *Appl. Therm. Eng.* **64**, 385–395 (2014)
21. Fengxia, H., Zhongbin, Z., Hu, H., Zemin, C.: Experimental study on the all-fresh-air handling unit with exhaust air energy recovery. *Energy Procedia* **152**, 431–437 (2018)
22. Park, D.Y., Yun, G., Kim, K.S.: Experimental evaluation and simulation of a variable refrigerant-flow (VRF) air-conditioning system with outdoor air processing unit. *Energy Build.* **146**, 122–140 (2017)
23. Aynur, T.N., Hwang, Y., Radermacher, R.: Integration of variable refrigerant flow and heat pump desiccant systems for the cooling season. *Appl. Therm. Eng.* **30**, 917–927 (2010)
24. Aynur, T.N., Hwang, Y., Radermacher, R.: Integration of variable refrigerant flow and heat pump desiccant systems for the heating season. *Energy Build.* **42**, 468–476 (2010)

25. Aynur, T.N., Hwang, Y., Radermacher, R.: Simulation comparison of VAV and VRF air conditioning systems in an existing building for the cooling season. *Energy Build.* **41**, 1143–1150 (2009)
26. Im, P., Malhotra, M., Munk, J.D., Lee, J.: Cooling season full and part load performance evaluation of variable refrigerant flow (VRF) system using an occupancy simulated research building. In: *Proceedings of the 16th International Refrigeration and Air Conditioning Conference at Purdue, West Lafayette, USA* (2016)
27. Lee, J.H., Yoon, H.J., Im, P., Song, Y.-H.: Verification of energy reduction effect through control optimization of supply air temperature in VRF-OAP system. *Energies* **11**(1), 49 (2018)
28. Khatri, R., Joshi, A.: Energy performance comparison of inverter based variable refrigerant flow unitary AC with constant volume unitary AC. *Energy Procedia* **109**, 18–26 (2017)
29. Trushliakov, E., Radchenko, M., Bohdal, T., Radchenko, R., Kantor, S.: An innovative air conditioning system for changeable heat loads. In: Tonkonogyi, V., et al. (eds.) *Grabchenko's International Conference on Advanced Manufacturing Processes. InterPartner-2019. LNME*, pp. 616–625. Springer, Cham (2020)

# **Energy Efficient Technologies and Industrial Ecology**



# Improvement of the Model System to Develop Eco-Friendly Bio-Utilization of Phosphogypsum

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**Abstract.** This paper focused on the modeling of the possibility of bacteria growth under medium that different content phosphogypsum (PG) doses for environmental protection purposes with special attention to the analysis of the effect of PG features underestimation of *E. coli* growth. The culture of *E. coli* is diluted with Lysogeny broth (LB) initially without adding PG to obtain an optical density at 600 nm (OD<sub>600</sub>) of 0.05. Study is carried out by adding different doses of PG (250 mg/200 mL LB; 500 mg/200 mL LB; 1000 mg/200 mL LB). The OD<sub>600</sub> is measured with the use of an absorption spectrophotometer. Under modeling PG feature effluence, several factors are identified that impact on bacteria growth and the general methodological approach to assessing the biochemical activity of PG is formed. The important direction for feature study the effect of PG use as a component of the medium for *E. coli* is the assessment of mutations and adaptive biochemical mechanisms, in particular, the possibility of biofilm formation. Microorganisms in biofilms are better adapted and much more resistant to high concentrations of various groups of xenobiotics. In some cases, the matrix itself is involved in bioremediation, sorbing and retaining toxic substances from the aqueous phase.

**Keywords:** Environmental protection · Phosphogypsum · Modeling influence · *E. coli* · Bioremediation

## 1 Introduction

The sharp increase in industrial products worldwide in recent decades has flowed a large number of toxic pollutants to nature, which creates a significant burden on the biosphere. Bioremediation today is one of the promising methods for solving the problem of toxic substances [1]. The development of environmentally friendly waste transformation is a priority task for the green economy in many countries, and biotechnology greatly helps in this direction. Addressing the environmental consequences of emergencies is often a difficult environmental task. A search is constantly underway for the best way to reclaim vast land areas, restore the productivity of water bodies contaminated. Biological objects, in particular bacteria, are actively involved in the conversion of compounds of various origin, including human-made.

The use of biological products in a classic form for wastewater treatment is complicated by the lack of increased buoyancy in cultures of hydrocarbon-oxidizing

microorganisms. The buoyancy of the bio-sorbent is provided by particles of hydrophobized peat, in the pores of which bacterial cells responsible for biological activity are immobilized. Biosorbent combines the physical method of eliminating oil pollution (sorption) with its further biological degradation by microorganisms. Another advantage of the biosorbent is the ability to quickly localize pollution on the surface of the water, preventing the spread in depth and on the surface of the water body [2].

Cleaning and disinfection of domestic and industrial wastewater is an important task of effective environmental management. This problem is especially acute at production facilities with insignificant water circulation, where the construction of their treatment facilities is not economically feasible, and the remoteness of the facilities does not allow to discharge effluents to treatment facilities of settlements or larger enterprises. The use of modular wastewater treatment plants can solve this problem [2–4].

The use of various methods of environmental protection based on biological processes is the most environmentally friendly approach. The current level of knowledge of the processes occurring in living cells and the development of hardware design can significantly increase the effectiveness of biological and chemical methods [1].

Thus, the development of technology for wastewater and chemical by-products treatment is urgently required. Bioremediation, mainly using bacteria is a valid strategy. The current biological method for wastewater treatment is well studied. But since the microbial community and their metabolism are complex to optimize, then the target is changed.

## 2 Literature Review

*Escherichia coli* is used as applications for a long time to produce useful substances and develop biosensors for monitoring environments. Its low maintenance cost, rapid cell growth a simple genome structure allow us to understand whole biochemical and molecular systems of this organism [5]. *E. coli* has a high biosynthetic capacity and can grow well in a defined mineral medium supplemented with a carbon source. As municipal solid waste (MSW) contains naturally high carbohydrates, it can be utilized as a carbon and energy source for bacterial cultivation [5]. In the study of Majida Khanafer et al. (2017), raw domestic sewage in Kuwait City contained about  $10^6$  mL<sup>-1</sup> colony-forming units of *Enterobacter hormaechei* subsp. *oharae* (56.6%), *Klebsiella* spp. (36%), and *E. coli* (7.4%) were detected. These coliforms isolated from the sewage grew successfully on a mineral agar medium with crude oil vapor as a sole source of carbon and energy [6]. The *E. coli* isolated from municipal wastewater showed characterized molecular marker patterns distinguishable from that in human and animal bodies [7].

Brewery spent grains (BSG), one of the by-products of brewery production, were used to study for hydrogen (H<sub>2</sub>) production by *E. coli*. *E. coli* BW25113 wild type strain, hydrogenase (Hyd)-negative mutant with deletions of genes encoding key subunits Hyd 1–4 ( $\DeltahyaB$ ,  $\DeltahybC$ ,  $\DeltahycE$ ,  $\DeltahyfG$ ), or that with  $\DeltahyaB \DeltahybC$  double mutant were investigated with regards to growth, acidification of the medium, redox potential kinetics and H<sub>2</sub> production when using BSG hydrolysate. Thus, the results lead to the development of approaches for the production of H<sub>2</sub> simultaneously with the processing of waste [8].

Effect of e-waste on *E. coli* PQ-37 genomic integrity was evaluated by Solomon E. Owumi et al. (2014) using the SOS chromo test. Damage to *E. coli* deoxyribonucleic acid (DNA) increased proportionally to the metal concentrations [9].

Phosphogypsum is the chemical by-product of phosphate fertilizer production. Huge dumps of the phosphogypsum are left in 52 countries, totalling in 5.6–7.0 billion tons [10]. The annual increase of its accumulation in the world reaches 120–130 million tons, and the mass fraction of utilization does not exceed 10%. At this time, more than 55 million tons were accumulated on the territory of Ukraine [11, 12].

Accordingly, it is necessary to determine the directions of processing and utilization of phosphogypsum as a secondary raw material resource, provided that the toxic component is bound to sparingly soluble compounds and removed from biochemical conversion cycles elements in the biosphere.

This paper focused on the modeling of the possibility of *E. coli* growth under medium that content different phosphogypsum doses for environmental protection purpose.

To achieve this aim, the following tasks were set:

- modeling and analysis of the effect of phosphogypsum features under estimation of *E. coli* growth;
- developing the methodological approach of the estimation of bacteria growth under the medium that included phosphogypsum.

### 3 Research Methodology

#### 3.1 Phosphogypsum Composition Analysis

The surface morphology of samples was observed by Scanning Electron Microscope (SEM) JSM-6510LA (JEOL Ltd., Japan) and the composition was analyzed by energy dispersive X-ray analysis (EDS).

#### 3.2 Methods of Bacteria Growth Investigation

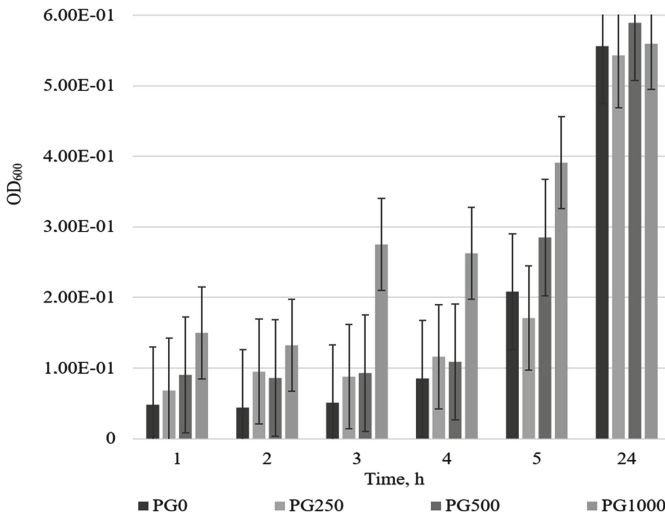
A single colony of *E. coli* was picked up, transferred into the Lysogeny broth (LB), and cultured overnight at 37 °C with constant shaking at 200 rpm. The cultured *E. coli* was diluted with fresh LB broth to obtain an optical density at 600 nm ( $OD_{600}$ ) of 0.05 as an initial inoculum. LB broths with different doses of phosphogypsum (PG) (PG250 = 250 mg/200 mL LB; PG500 = 500 mg/200 mL LB; PG1000 = 1000 mg/200 mL LB, 25 mL each in 50 mL culture tube) were prepared, with added 100  $\mu$ L of initial *E. coli* inoculum and cultured at 37 °C with constant stirring 200 rpm. Triplicate 100  $\mu$ L aliquots were removed every hour for 5 h and after 24 h from each condition, and the  $OD_{600}$  values were measured using a multi-spectrophotometer 96-well plate reader (Synergy H1, Gen5 version 2.05) (BioTek® Instruments, Japan). Bacterial growth experiments were repeated 5 times independently to analyze the effect PG on bacterial growth.

Modeling and processing of experimental data were carried out using Microsoft Excel and bioinformatics databases such as KEGG: Kyoto Encyclopedia of Genes and Genomes.

## 4 Results

### 4.1 Modeling and Analysis of the Effect of Phosphogypsum Features under Estimation of *E. coli* Growth

Figure 1 shows the growth of *E. coli* in LB broth with different doses of PG.



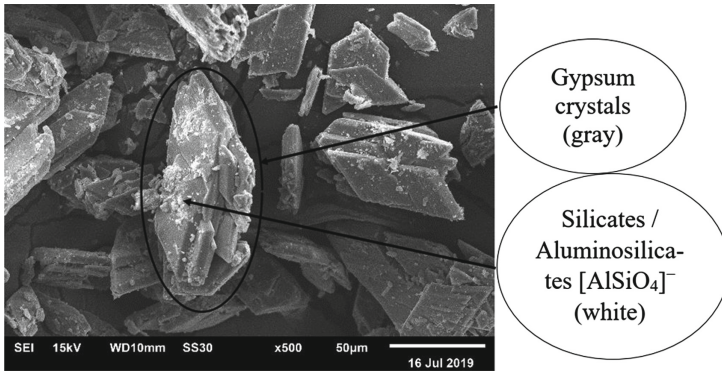
**Fig. 1.**  $OD_{600}$  cultural suspension at different doses of Phosphogypsum.

To obtain these data, the average values of the change in the  $OD_{600}$  value in a series of experiments were found. At the beginning of the experiment, when analyzing the same sample (measuring one sample three times at different doses of PG), very different  $OD_{600}$  values were observed under the same conditions, since the precipitation of the PG components during mixing influenced the measurement readings. It was decided to take into account the primary  $OD_{600}$  of the culture medium with different PG concentrations. But in subsequent measurements, there was still a significant variation in the readings of the  $OD_{600}$  value. This was facilitated by the rapid sedimentation of particles of PG components. Therefore, in further experiments, the only supernatant was taken. During the first 5 h of *E. coli* cultivation, an  $OD_{600}$  increase was observed in samples with PG compared with the culture medium without its addition.

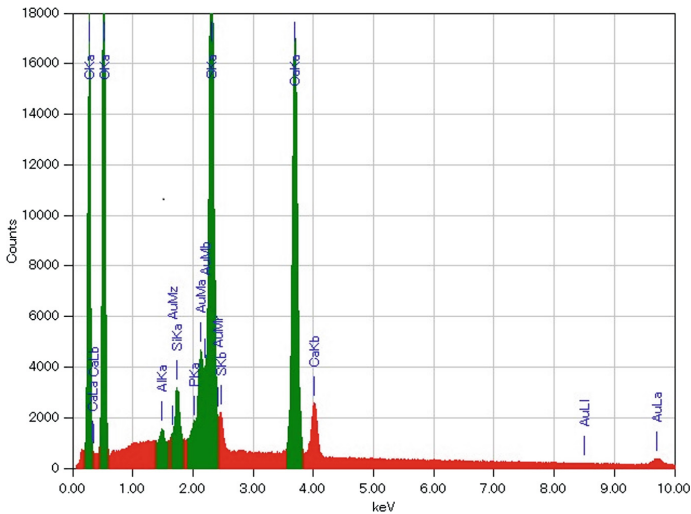
It's a very important task in developing the methodological approach for assessing the biochemical activity of PG with understanding influence chemical features of PG under metabolic pathways and  $OD_{600}$  measurement.



Since PG is a poorly soluble compound, its solubility in water does not exceed 1000 mg/L. Such a low solubility in water is since PG is formed from gypsum crystals, and it also has inclusions of aluminosilicates (see Fig. 2). Ca, S, Si, Al, P are the most represented elements in the PG composition (see Fig. 3).



**Fig. 2.** SEM images of phosphogypsum sample.



**Fig. 3.** EDS spectra of the field (Au is presented only under the metallization process of the sample).

But the metabolic activity of bacteria can affect the solubility of PG. Several factors influencing on the bacterial growth under this system are discussed; (i) the initial increase in the turbidity of the culture medium with different doses of PG and the rapid deposition of PG components on the bottom of the tube with a decrease in the turbidity;

(ii) partial splitting of the components of PG in the medium during the time of cultivation of *E. coli* and reducing sediment; (iii) after 24 h, tubes with culture media with PG and without it had approximately the same turbidity (see Fig. 4) and this was confirmed when evaluating the optical density (see Fig. 1).

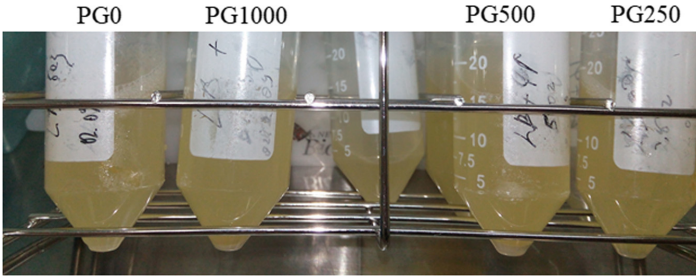


Fig. 4. Photography tubes after 24 h of *E. coli* cultivation.

Thus, the important task is the correct assessment of the effect of PG properties on a possible increase in the turbidity of the nutrient medium of some samples when raising this precipitate with stirring, which affects the evaluation of the experimental results.

Such effects of the influence of PG can be seen on the three-dimensional surface of the change in the OD<sub>600</sub> of the culture suspension (Fig. 5), which indicates the need for a series of experiments taking into account the above-mentioned observed properties in the ‘culture-medium- PG’ system. This will allow the most objective assessment of PG effect on *E. coli* growth.

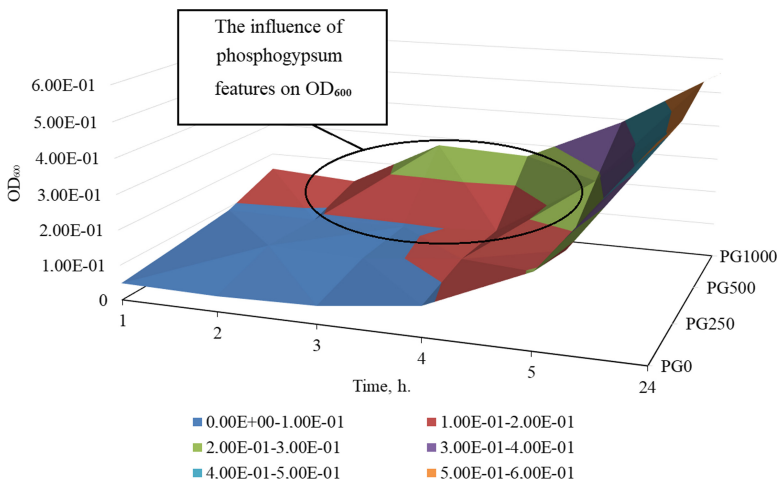


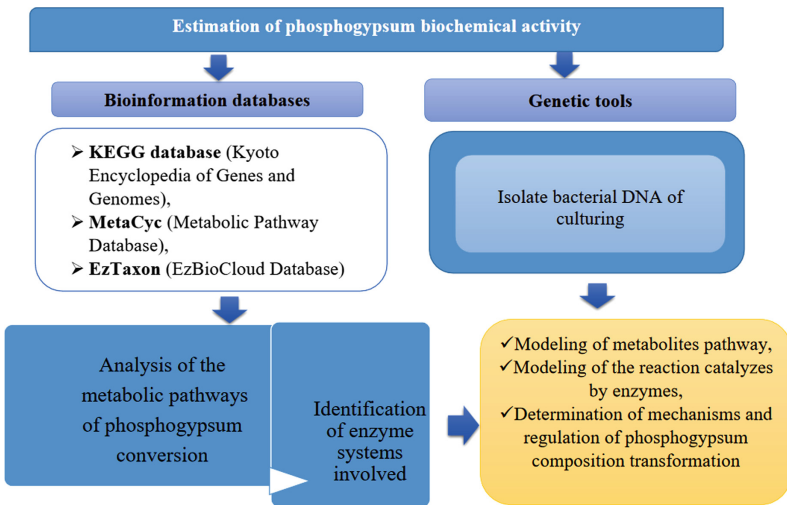
Fig. 5. 3D surface under the ‘culture-medium- PG’ system.

## 4.2 Developing Methodological Approach of Estimation Bacteria Growth Under Medium that Included Phosphogypsum

Figure 6 shows the general methodological approach for assessing the biochemical activity of PG. It is also important to evaluate the change in the solubility of PG components upon exposure to metabolites.

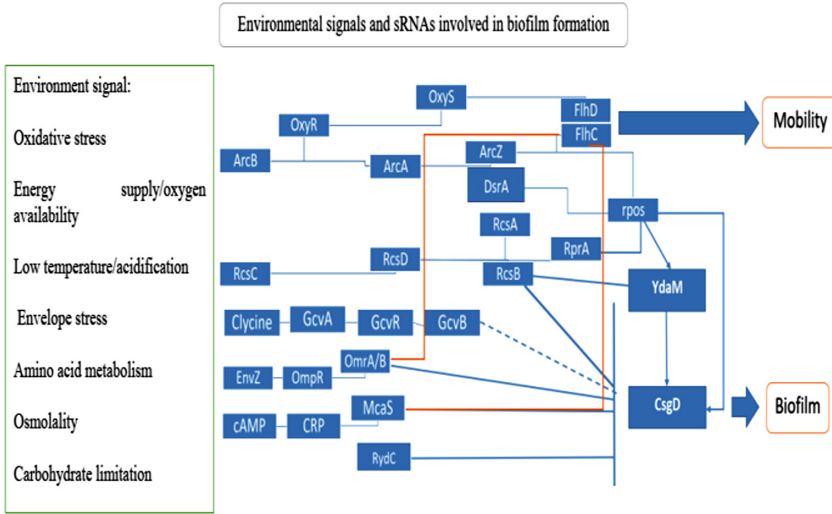
The methodological idea of model systems to develop eco-friendly bio-utilization of PG is as follow: (i) select biotechnologically amenable bacteria as models; (ii) check bacteria responses against PG; (iii) analyse their responses genetically and theoretically; (iv) apply these findings to the bacteria which are used in the plant of wastewater treatment.

Under this research, we use *E. coli* as a model to estimate its response against PG effluence. It should be noted that a separate study of the metabolic pathways of strict anaerobes is necessary. For example, sulfate-reducing bacteria (SRB) that use sulfate as an electron acceptor and SRB can be involved in a consortium with methanogenic bacteria during anaerobic digestion.



**Fig. 6.** The general model of estimation bacteria growth under medium that included phosphogypsum.

Thus, the important direction for assessing the possibility of using PG as a component of the medium for *E. coli* is the assessment of mutations and adaptive biochemical mechanisms, in particular, the possibility of biofilm formation (Fig. 7).



**Fig. 7.** Model of biofilm formation factors. Based on data from the KEGG database ([https://www.kegg.jp/kegg-bin/show\\_pathway?ko02026+K07677](https://www.kegg.jp/kegg-bin/show_pathway?ko02026+K07677)).

Figure 7 shows the following notation according with KEGG database: ArcB is a two-component system, OmpR family, aerobic respiration control sensor histidine kinase; ArcA is a two-component system, OmpR family, aerobic respiration control protein; ArcZ is a small regulatory RNA; OxyR is a LysR family transcriptional regulator, hydrogen peroxide-inducible genes activator; OxyS is a small regulatory RNA; DsrA is a non-coding RNA that regulates both transcription, by overcoming transcriptional silencing by the nucleoid-associated H-NS protein, and translation, by promoting efficient translation of the stress sigma factor; small regulatory RNA; FlhD is a flagellar transcriptional activator; FlhC is a flagellar transcriptional activator; RcsC is a two-component system, NarL family, capsular synthesis sensor histidine kinase; RcsD is a two-component system, NarL family, sensor histidine kinase; RcsA is a LuxR family transcriptional regulator, capsular biosynthesis positive transcription factor; rpos is a RNA polymerase nonessential primary-like sigma factor; YdaM is a diguanylate cyclase; CsgD is a LuxR family transcriptional regulator, csgAB operon transcriptional regulatory protein; GcvA is a LysR family transcriptional regulator, glycine cleavage system transcriptional activator; GcvR is glycine cleavage system transcriptional repressor; EnvZ is a two-component system, OmpR family, osmolarity sensor histidine kinase; OmpR is a two-component system, OmpR family, phosphate regulon response regulator; OmrA/B is a small regulatory RNA; CRP is a FNR family transcriptional regulator, cyclic AMP receptor protein; McaS is a mast cell activation syndrome, small regulatory RNA; RydC is a small regulatory RNA.

*E. coli* showed that the type of bacterial motility is necessary for the formation of biofilms. The bacterial mobility provided by the flagella is necessary to establish a connection between the bacteria and the surface, while the mobility provided by the fimbriae is necessary for the formation of microcolonies. When establishing the initial

interaction, a stable connection between bacteria and the surface of the substrate is ensured due to specific proteins of the cell membrane, adhesins [13].

Biofilms, in this case, are more preferable than planktonic cultures, because, as mentioned earlier, this type of community is more resistant to changing environmental conditions. Microorganisms in biofilms, being protected by a layer of the extracellular matrix, are better adapted and much more resistant to high concentrations of various groups of xenobiotics, in particular, chlorine and nitrogen-containing aromatic compounds. In some cases, the matrix itself is involved in bioremediation, sorbing and retaining toxic substances from the aqueous phase.

Thus, the development of an approach to the treatment of wastewater and chemical wastes such as PG for coagulation and aggregation to achieve the effective removal of biogenic and toxic substances using multidimensional biofilms containing, in addition to hydrocarbon-oxidizing bacteria, other ecologically trophic groups, for example, *E. coli*, is one of the possible areas for further research.

## 5 Conclusions

1. Under modeling PG feature effluence several factors were identified that impact on bacteria growth: (i) the initial increase in the turbidity of the culture medium with different doses of PG and the rapid deposition of PG components on the bottom of the tube with the decrease in the turbidity; (ii) partial splitting of the components of PG in the medium during the time of cultivation of *E. coli* and reducing sediment; (iii) after 24 h, tubes with culture media with PG and without it had approximately the same turbidity and this was confirmed when evaluating the optical density.
2. The methodological approach was developed for assessing the biochemical activity of PG for understanding influence chemical features under metabolic pathways and OD<sub>600</sub> measurement. The important direction for assessing the effect of PG use as a component of the medium for *E. coli* is the assessment of mutations and adaptive biochemical mechanisms, in particular, the possibility of biofilm formation. It is also important to evaluate the change in the solubility of PG components upon exposure to metabolites. It should be noted that a separate study of the metabolic pathways of strict anaerobes is necessary for providing a special technology model of implementation on the wastewater treatment plant.

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## References

1. Nozhevnikova, A.N., Bochkova, E.A., Plakunov, V.K.: Multi-species biofilms in ecology, medicine and biotechnology. *Mikrobiologiya* **84**(6), 623–644 (2015). (in Russian)
2. Pystina, N.B., Listov, E.L., Balakirev, I.V., Nikishova, A.S., Lipnik, S.I.: The use of modern biotechnology in solving urgent environmental problems of the oil and gas complex. *Sci. Tech. Collect. News Gas Sci.* **2**(13), 113–117 (2013). (in Russian)

3. Corcoran, E., Nellemann, C., Baker, E., Bos, R., Osborn, D., Savelli, H. (eds.): Sick Water? The Central Role of Waste-Water Management in Sustainable Development. A Rapid Response Assessment. United Nations Environment Programme, UN-HABITAT GRID-Arendal, Norway (2010)
4. Connor, R.: The United Nations World Water Development Report 2015: Water for a Sustainable World. UNESCO, Paris (2015)
5. Rosander, E., Svedendahl Humble, M., Veide, A.: Municipal solid waste as carbon and energy source for *Escherichia coli*. *Adv. Recycl. Waste Manag.* **1**(2), 2–8 (2016). <https://doi.org/10.4172/2475-7675.1000114>
6. Khanafer, M., Al-Awadhi, H., Radwan, S.: Coliform Bacteria for Bioremediation of Waste Hydrocarbons. *Hindawi BioMed Res. Int.* (2017). <https://doi.org/10.1155/2017/1838072>
7. Zhi, S., Banting, G.S., Ruecker, N.J., Neumann, N.F.: Stress resistance in naturalised waste water *E. coli* strains. *J. Environ. Eng. Sci.* **12**(2), 42–50 (2017). <https://doi.org/10.1680/jenes.16.00021>
8. Poladyan, A., Trchounian, K., Vassilian, A., Trchounian, A.: Hydrogen production by *Escherichia coli* using brewery waste: optimal pretreatment of waste and role of different hydrogenases. *Renewable Energy* **115**(C), 931–936 (2018)
9. Owumi, S.E., Odunola, O.A., Gbadegesin, M.A., Ayoola, B., Onuchukwu, E.: Effect of electronic waste on *E. coli* genomic integrity: a possible role for metal induced carcinogenesis. *Toxicol. Environ. Chem.* **96**(10), 1581–1591 (2014). <https://doi.org/10.1080/02772248.2015.1029480>
10. Hermann, L., Kraus, F., Hermann, R.: Phosphorus processing – potentials for higher efficiency. *Sustainability* **10**, 1482 (2018)
11. Chernysh, Y., Balintova, M., Plyatsuk, L., Holub, M., Demcak, S.: The influence of phosphogypsum addition on phosphorus release in biochemical treatment of sewage sludge. *Int. J. Environ. Res. Public Health* **15**, 1269–1283 (2018)
12. Plyatsuk, L.D., Chernysh, Y.Y., Ablicieva, I.Y., Yakhnenko, O.M., Battaltsev, E.V., Balintova, M., Hurets, L.L.: Remediation of soil contaminated with heavy metals. *J. Eng. Sci.* **6**(1), H1–H8 (2019). [https://doi.org/10.21272/jes.2019.6\(1\).h1](https://doi.org/10.21272/jes.2019.6(1).h1)
13. Svjetlana, M., Vrane, J.: Characteristics and significance of microbial biofilmformation. *Periodicum biogorum* **109**(2), 115–121 (2007). [https://bib.irb.hr/datoteka/314210.9\\_Maric\\_Vranes-Periodicum.pdf](https://bib.irb.hr/datoteka/314210.9_Maric_Vranes-Periodicum.pdf)



# Influence of High-Octane Bioadditives on Physical and Chemical Properties of Low-Octane Gasoline

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**Abstract.** The problem of environmental safety of road transport has become an integral part of the security of Ukraine. The annual increase in vehicle emissions into the atmosphere requires the strengthening of environmental requirements for commercial fuels and exhaust gases of internal combustion engines. Modern cars require high-octane fuel with anti-knock properties, which are characterized by an experimental octane number of 92.95 and 98. For cars with gasoline engines with a compression ratio of up to 8, which are present in the fleet of Ukraine, as well as for trucks of the previous generation, there is a need for gasoline with a lower octane number. The presence of imported cars requires the production of gasoline, which would meet environmental requirements and would have a low cost. In this regard, increasing interest in the use of bioadditives, that would improve the environmental and operational properties of the fuel. World experience shows that the use of 10–15% bioadditives in the gasoline mixture does not have a negative impact on the technical and operational performance of the internal combustion engine. Therefore, the study of the influence on the physical and chemical properties of low octane gasoline is relevant.

**Keywords:** Gasoline · Operational properties · Quality · Ecological purity · Bioadditives

## 1 Introduction

The main share in the market of passenger cars in Ukraine is occupied by imports, which share in 2017 was more than 95% of capacity. For 9 months in 2018, the share of used cars has been 63% [1, 2]. According to [3] the number of new cars produced in 2017, is relatively small on the roads of Ukraine - only 150 thousand.

Modern cars require high-octane fuel with anti-knock properties, which are characterized by a research octane number of 92.95 and 98. For cars with gasoline engines with a compression ratio of up to 8, which are present in the fleet of Ukraine, as well as

for trucks of the previous generation, there is a need for gasoline with a lower octane number. The use of high-octane gasoline in cars with a compression ratio of up to 8 is the cause of a number of breakdowns: failure of the piston fingers, painting liners connecting rod and main bearings; cracking of insulation and burnout of contacts of spark plugs; burnout of the bottoms of pistons; burnout of working facets of exhaust valves and their seats; burnout of gaskets between the head and the cylinder block; burnout of piston rings and their increased wear. However, environmental safety and the low cost of such gasoline remain one of the priority requirements in the production of gasoline.

The presence of imported cars requires the production of gasoline, which would meet environmental requirements and would have a low cost. In this regard, there is growing interest in the use of bioadditives, which would improve the environmental and operational properties of the fuel. World experience shows that the use of 10–15% bioadditives in the gasoline mixture does not have a negative impact on the technical and operational performance of the internal combustion engine. In addition, the use of such fuel has more advantages, because it is more environmentally friendly, it generates less emission from combustion. Biofuels can be adapted to existing engine designs, which will be well used in all conditions. At the same time, such fuel is better for engines, it reduces the overall cost of controlling engine pollution and, therefore, its use requires fewer maintenance costs. At the same time, modern requirements for gasoline are that gasoline must provide a homogeneous fuel-air mixture of the required composition at all temperature conditions. In this case, the fuel should evaporate well, have a small surface tension, good starting properties and provide a quick warm-up of the cold engine. To do this, the fuel must have a high heat of combustion, burn completely, without detonation in all modes of operation of the engine. Modern cars require high-octane fuel with anti-knock properties characterized by motor octane 92.95 and 98. At the same time, in the fleet of Ukraine, there are cars with gasoline engines with a compression ratio of up to 8.5, as well as trucks of the previous generation, which require the use of low-octane gasoline.

## 2 Literature Review

World experience shows that the use of 10–15% biodiesel in a gasoline mixture does not have a negative impact on the technical and operational performance of the internal combustion engine [4]. In addition, there are more advantages in the use of such fuel, since it is a more environmentally friendly type of fuel when it is used; less emission is generated during combustion. Biofuels can be adapted to existing engine designs, which will be well used in all conditions. At the same time, such fuel is better for engines, it reduces the overall cost of controlling engine pollution and, therefore, its use requires fewer maintenance costs. At the same time, modern requirements for gasoline are that gasoline must provide a homogeneous fuel-air mixture of the required composition at all temperature conditions. In this case, the fuel should evaporate well, have a small surface tension, good starting properties, and provide a quick warm-up of the cold engine. To do this, the fuel must have a high heat of combustion, burn completely, without detonation in all modes of operation of the engine.



Many bioadditives and fuel compositions based on them have been patented and used in the world [5]. The experience of using high-octane compounds of various classes has shown that the most promising among them are oxygen-containing applications, or oxygenates [6–8]. In the previous publication, we studied the effect of ethanol on the performance properties of gasoline [9].

The problems of efficient and economical use of energy resources and expansion in the structure of the total energy consumption of renewable energy sources have been widely covered in scientific works of foreign scientists: Ajanovic A., Bentivoglio D., Rasetti M., Popp J., Lakner Z., Harangi-Rákos M., Fári M., Tyner W. and others [10–13]. Alcohol fuels have high antetonation properties, so they are used in carburetor engines with forced ignition. Also, alcoholic fuels provide a high-efficiency factor for engine workflow throughout the range of working mixtures. This reduces the specific energy consumption per unit of power. It is important to reduce the number of toxic components in exhaust gases, nitrogen oxides particularly.

### 3 Research Methodology

Estimation of parameters of operational properties for mixed fuels is performed using standard methods of investigation of the physical and chemical properties of fuels, which are standard for both oil and alternative fuels [14]. The processing of experimental results was carried out on the software [15].

Density, sulphur and oxygen content, molecular weight, actual resin content, refractive index, the heat of combustion and evaporation were determined in the gasoline fractions and bioadditives used for research. All these indicators were determined by standard methods. The structure-group composition of gasoline was determined by chromatographic method on the gas chromatograph Agilent-6890 with flame ionization detector, as well as by chromate mass spectrometry on the mass spectrometer LKB-2091. Octane number by research and motor methods was determined according to SSTU ISO 5164:2005. When adding additives to gasoline, their octane numbers were determined by the experimental method. Based on the results of the conducted dossier the recipe of petrol A-80 was suggested. The properties of the obtained gasoline with bioadditives were checked for compliance with the requirements of SSTU 7687:2015 according to the most important indicators, which were determined by standard methods.

### 4 Results

Gasoline fractions obtained at refineries at atmospheric distillation plants have low octane numbers, in the range of 65–75 according to the research method [16]. At low octane values, the use of such fuel is fraught with negative consequences for the engine due to the detonation of the fuel. Among the most common there are premature wear of valves and seats, as well as residues of carbon on the walls and surfaces. Therefore, the octane number must be suitable for a particular engine, so it is relevant to use various methods to increase the octane number of gasoline. In the traditional scheme of the

refinery, the catalytic reforming process is used to increase the octane number of straight-run gasoline, and its final product - the reformat is added to the gasoline as the main source of aromatic hydrocarbons and benzene (the aromatics content in the reformat is 60–70%, including benzene 2–7% by weight.) [17]. The reforming process itself is quite energy-intensive using expensive platinum catalysts, and the yield of the target products is 80–84% by weight. To reduce the proportion of aromatic hydrocarbons and benzene, various options for processing reformation products are offered, but they lead to additional costs. However, the requirements of the standards regulate the content of aromatic hydrocarbons in gasoline to 35%, benzene to 1% [18]. A drastic reduction of aromatic hydrocarbons, including benzene, can be achieved by reducing the proportion of reforming products and using octane-boosting components to preserve the octane number of gasoline at the required level [6]. In this regard, there is growing interest in the use of bio supplement, which would improve the environmental and operational properties of fuel and be economically feasible when adding to gasoline with a low octane number [19].

The use of bio-alcohol as a fuel or fuel additive has long been known: in 1914 it was proved that the transition from gasoline to alcohol was possible, and in 1934 in Europe, more than 2.65 million m<sup>3</sup> of alcohol-benzine mixtures were produced [20].

The advantage of alcohol-containing fuels is reducing the amount of carbon monoxide, nitrogen oxides, and soot in the exhaust gases of engines. In addition, alcohols have high anti-knock properties and are the most effective anti-knock additive. Alcohol-gasoline mixtures are similar in motor properties to traditional petroleum fuels. Despite the lower heat of combustion, such compositions provide work on impoverished mixtures, so the increase in fuel consumption, in this case, is insignificant: the average re-consumption of fuel ethanol containing is 5%. As a result of the use of alcohol, not only carbon monoxide and hydrocarbon emissions are reduced, but also the emission of nitrogen oxides from the exhaust gases of cars.

Bioesters are promising motor fuels. In comparison with alcohols, their advantages are that the oxygen content in their molecules is two times lower. The lower heat of combustion is much higher than in alcohol. Esters are corrosive inactive or low active, almost insoluble in water, environmentally safer, and detonation resistance is inferior to alcohol. The list of oxygenates that was used is large: bioesters-methyl-tert-butyl, methyl-tert-amyl, ethyl-tert-butyl, diisopropyl and others; biospirts-methanol, ethanol and some others.

The purpose of this work is to assess the effect of bio-additives on the physical and chemical properties of gasoline fractions obtained from various oils, to determine the necessary amount of bio-additives to achieve the octane number 80.

Gasoline fractions were obtained during the distillation of oil from the Rozhniavtske deposit (fr. 54–200), Styniavske deposit (fr. 49–200 C), mixtures of Western Ukrainian oil deposits and mixtures of East Ukrainian oil deposits. As for supplements methanol, ethanol, isopropanol, isobutanol, methyl tertiary butyl ether (MTBE) and ethyltertbutyl ether (ETBE) were used. Biomethanol increases the octane number of gasoline improves the combustion process of fuel and has a very high heat of evaporation. For its production, it is possible to use vegetables reducing raw materials, which can be converted into synthesis gas (biomass, biogas, agricultural and wood waste). Due to the high octane number, which allows increasing the compression ratio

to 16, methanol is used for refueling racing motorcycles and cars. The main advantage of gasoline-methanol fuels is the reduction of nitrogen oxides, carbon monoxide, and other harmful substances in the exhaust gases of cars. However, the use of methanol in many countries is prohibited due to its high toxicity, volatility, and increased hygroscopicity, which also creates a number of technical difficulties when using alcohol-gasoline mixtures [21, 22]. Bioethanol is a less hygroscopic product, which has more heat of combustion and less heat of evaporation. It is significantly less toxic than methanol. Its advantage also lies in the fact that it is made from renewable raw materials. The main producer of ethanol in the world is Brazil, the second in the volume is the United States. The use of fuels with ethanol is successfully implemented worldwide. In the USA since 1978 gasohol fuel with an ethanol content of 10% has been produced, in Brazil since 1930 fuel mixes contained 2–8% ethanol have been used. About a quarter of the modern car fleet of this country runs on alcohol-based fuel, which contains gasohol and is gasoline with 20% pure ethanol [21]. In Sweden, Finland, gasoline is operated with 85% ethanol. As of 2012, the main producers of bioethanol are the United States ( $\approx 40$  million t/g) mainly from corn and Brazil - from sugar cane ( $\approx 15$  million t/g) [21]. In Western Europe, the main producers of bioethanol are France, Sweden, Spain, Germany.

However, ethanol has a number of disadvantages: absolute ethanol is hygroscopic (although to a lesser extent than methanol); corrosive; negatively affects rubber and plastic parts. Biobutanol can completely replace gasoline in internal combustion engines. In terms of technical characteristics, biobutanol is superior to ethanol: the heat of combustion is 25% greater than that of ethanol and 10% greater than that of gasoline. It is safe to use because it evaporates 6 times less than ethanol and is 13.5 times less volatile than gasoline; it does not cause corrosion [23]. Butanol has a low saturated vapor pressure and its mixture with gasoline is not as hygroscopic. It provides a better fuel economy than gasoline-ethanol blends. Butanol will also provide lower greenhouse gas emissions into the atmosphere. However, obtaining this type of fuel is quite difficult. According to analysts, butanol can become an important part of the fuel market for transport. However, currently, its production is at the initial stage of development. Isopropanol is characterized by high maximum allowable concentration and octane rating values, has good physical stability in mixtures with gasoline, and also provides physical stability of gasoline-ethanol mixtures [24]. The addition of 6% isopropanol increases the octane number by the motor method of the straight-run fraction of gasoline by 13, and the octane number by the experimental method by 17 points. When isopropanol is added in an amount of more than 6%, its effectiveness decreases as an antidetonator [25]. Methyl tert-butyl ether (MTBE) is widely used in the production of gasoline as a high-octane component (octane number according to the research method 115–135 units) and contributes to more complete combustion of motor fuel without the formation of solid deposits on the cylinder walls of the internal combustion engine and prevent corrosion of the metal surface. In the EU the maximum legal content of MTBE in gasoline is 15% [8]. The addition of 10–15% MTBE increases the octane number of gasoline by an average of 6–12 units [26]. Currently, the issue of environmental safety of MTBE application is very acute, in connection with which its homologues-ethyl and butyl esters of tert-butanol are considered as an alternative additive.

Ethyltretbutyl ether (ETBE) is a clear, colorless or pale yellow liquid, an organic compound with a characteristic ethereal odor, obtained from ethanol (47% vol.) and isobutylene (53% Vol.). The addition of ETBE to gasoline up to 15% is allowed by the Technical regulations. ETBE on an industrial scale was first used in 1992 in France and since that time the popularity of its use as an antidetonator has been steadily growing [27, 28]. The undoubted advantage of ETBE is its biodegradability in nature, as well as the possibility of using ethyl alcohol obtained from vegetable raw materials (bioethanol) as a raw material. Physical and chemical parameters of bio-applications to gasoline are presented in Table 1. The applications have sufficiently high calorific value, high octane numbers, low saturated vapour pressure, which will improve the combustion of the combustible mixture.

**Table 1.** Physical and chemical parameters of bioapplications to gasoline.

Indicators	Oxygenates					
	Methanol	Ethanol	Iso-propanol	Iso-butanol	MTBE	ETBE
Density at 20 °C, kg/m <sup>3</sup>	795	790	780	802	742	746
Evaporation combustion heat kJ/kg	22707	26945	33300	35690	33200	30600
Flash point (in closed crucible), °C	6,5	12	13	27	-28	-
Octane number						
- by research method	122	121	117	108	115	118
- by the motor method	93	97	95	91	97	102
Saturated vapor pressure, kPa	35	17	13	9,7	53,0	34,5
Oxygen content, % vol	50,0	34,78	32,0	21,6	16,18	15,38

Physical and chemical parameters of gasoline fractions of various oils used for experiments are presented in Table 2. Gasoline fractions straight-bottomed from the Rozhniativske oil deposit (fr. 54–200), Styniavske deposit (fr. 49–200 C), mixtures of Western Ukrainian oil fields and oil mixtures of Eastern Ukrainian fields are characterized by a low sulphur content, a sufficiently high content of aromatic and naphthenic hydrocarbons.

The density of gasoline fractions of oils is 753–769 kg/m<sup>3</sup>. Water-soluble alkalis and acids are absent. The octane number of these fractions is determined by the experimental method is not high. For a number of mini refineries that do not have production facilities to increase the octane number of gasoline fractions, it is relevant to use high-octane applications that are environmentally safe and do not contain benzene, aromatic hydrocarbons, sulphur compounds. The above-mentioned biological applications were added to straight-run gasoline in the amount reaching the octane number 80. The results are presented in Table 3.

**Table 2.** Physical and chemical parameters of gasoline fractions of various oils.

Name of the indicator	Rozhniatvskie deposit Fraction 54–200 °C	Styniavskie deposit Fraction 49–200 °C	A mixture of West-Ukrainian oils	The mixture of Eastern-Ukraine. oils
Sulphur content, % wt.	0,021	0,017	0,016	0,014
Group composition, % mass.:				
- paraffin hydrocarbons, % wt.	53,12	51,23	38,6	36,2
- naphthenic hydrocarbons, % wt.	28,02	27,59	34,2	38,6
- olefin hydrocarbons, % wt.	0,11	0,15		
- aromatic hydrocarbons, % by weight.	18,75	21,03	27,2	25,2
Refractive index	1,4275	1,4274	1,4302	1,4316
Density, kg/m <sup>3</sup>	763	753	769	754
Molecular weight	126,5	118		
Actual resins, mg/100 cm <sup>3</sup>	23	27	19	21
The octane number of the experimental method	65	63	66	67

**Table 3.** Determination of octane numbers of mixed gasoline using straight-run gasoline of various oils and alcohols.

Addition to gasoline	Octane number	The amount of additive to reach octane number 80, %			
		Gasoline Styniava (ON = 63)	Gasoline Rozhniativ (ON = 65)	Gasoline mixture of West-Ukrainian oils (ON = 66)	Gasoline mixture of Eastern-Ukrainian oils (ON = 67)
methanol	122	28,8	26,3	25,0	23,6
ethanol	121	29,3	26,8	25,5	24,1
isopropanol	117	31,5	28,8	27,5	26,0
isobutanol	108	37,8	34,9	33,3	31,7
MTBE	118	30,9	28,3	26,9	25,5
ETBE	119	30,4	27,8	26,4	25,0

Optimal formulations of low octane gasoline with various bio-applications are proposed based on the prices of the components of such mixtures and the requirements for their quality (Table 4).

**Table 4.** Recommended recipe for gasoline with octane number = 80.

Compound mixtures	Octane number	% content	The octane number of the mixture	Price of the component	Price of the mixture
Straight-run gasoline	65	57	80,82	15000	20628
Reformat	95	29		27200	
isobutanol	108	4		26000	
MTBE	119	10		31500	

The lowest cost will be in a mixture of straight-run gasoline and Isobutanol, even though its content in the mixture is the highest (Table 5).

**Table 5.** Compliance of indicators of the received gasoline to requirements according to SSTU 7687:2015.

Name of indicator	Value of norm	Identified indicators	Research method
Octane number by the experimental method	80	80,5	SSTU ISO 5164
Crowded steam in summer, kPa	45–80	68,1	SSTU EN13016-1
Density at 15 °C, kg/m <sup>3</sup> , within	720–775	762	SSTU EN ISO3675
Fractional composition:			
- the volumetric fraction of evaporation at 70 °C, %	20,0–50,0	32,0	According to SSTU 2177
- the volume of evaporation at 100 °C, %	46,0–71,0	64,0	
-volume of evaporation at temperature 150 °C, %	75,0	76,0	
- the boiling point is finite, °C, not higher	210	203	
- volume fraction of residual after boiling, %, not more	2	1,5	
Sulphur content, mg/kg	10	48	SSTU EN ISO 20884
Volume fraction of aromatic hydrocarbons, %	35	34	SSTU 7686
Volume fraction of benzene, %	1	0,9	SSTU EN12177
Mass fraction of oxygen, %	2,7	2,7	SSTU EN 12177
The concentration of actual resins, mg/100 cm <sup>3</sup>	5	4	SSTU GOST 1567
Corrosion on a copper plate (3 h at 50 °C) class	1	1	SSTU EN ISO 2160

## 5 Conclusions

The use of octane-boosting applications such as Isobutanol and MTBE, as well as reformat, increases the octane number of straight-run gasoline, while the cost of gasoline remains competitive. Gasoline fractions obtained during the distillation of oil from the Rozhniativskie deposit (fr. 54–200 °C), Styniavskie deposit (fr. 49–200°C), mixtures of Western Ukrainian oil fields and mixtures of East Ukrainian oil fields.

Biofuels in the amount of 10 and 20% was added to straight-run gasoline.

Optimal formulations of low octane gasoline with various bio-applications are proposed based on the prices of the components of such mixtures and the requirements for their quality. The lowest cost was in a mixture of straight-run gasoline and Isobutanol despite the fact that its content in the mixture is the highest. The amount of Isobutanol in the composite mixture should be left in the amount of 4%, MTBE in the amount of 10%. Then the total oxygen content will be within acceptable norms. The content of the reformat in the mixture is set at 29%.

Having analyzed the physical and chemical parameters of the resulting gasoline mixture, we concluded that this type of fuel meets the requirements of SSTU 7687:2015, i.e. it can be used in gasoline engines of motor vehicles.

## References

1. Analysis of the Ukrainian passenger car market. <https://pro-consulting.ua/issledovanie-rynka/analiz-rynka-legkovyh-avtomobilej-ukrainy-2018-god>. Accessed 28 Oct 2019
2. Dyma, O.: Passenger car market and prospects of its development in Ukraine. Bulletin of Lviv commercial Academy. Econ. Ser. **46**, 44–49 (2014)
3. Named the exact number of cars in Ukraine and their average age, [https://auto.24tv.ua/nazvana\\_tochna\\_kilkist\\_avtomobiliv\\_v\\_ukraini\\_ta\\_yikh\\_serednii\\_vik\\_n6262](https://auto.24tv.ua/nazvana_tochna_kilkist_avtomobiliv_v_ukraini_ta_yikh_serednii_vik_n6262). Accessed 26 Oct 2019
4. Borzaiev, B., Kerpov, S., Kapustin, V.: Multifunctional additives to automobile gasoline. Chem. Technol. Fuels Oils **2**, 18–20 (2007)
5. Chen, H., Yang, L., Zhang, P., Harrison, A.: The controversial fuel methanol strategy in China and its evaluation. Energy Strat. Rev. 28–33 (2014)
6. Nguyen, V.T.: Production of motor gasoline with improved environmental properties: in relation to the conditions of the Republic of Vietnam. Ph.D thesis, Ufa (2008)
7. Rasskazchikova, T., Kapustin, B., Karpov, S.: Ethanol as a high-octane additive to automotive gasoline. Fuel Oil Chem. Technol. **4**(524), 3–7 (2004)
8. Oparina, L.A., Kolyvanov, N.A., Gusarova, N.K., Saprygina, V.N.: Oxygenate additive to fuel based on renewable raw materials. Appl. Chem. Biotechnol. 8(1), 19–34 [in Russian]. <https://doi.org/10.21285/2227-2925-2018-8-1-19-34>. Proceedings of Universities
9. Tkachuk, V., Rechun, O., Merezhko, N., Bozhydarnik, T., Karavaiev, T.: Assessment of the quality of alternative fuels for gasoline engines. In: Ivanov, V., et al. (eds.) Advances in Design, Simulation and Manufacturing. DSMIE-2019. Lecture Notes in Mechanical Engineering, pp. 871–881. Springer, Cham (2019). [https://doi.org/10.1007/978-3-030-22365-6\\_46](https://doi.org/10.1007/978-3-030-22365-6_46)
10. Veloso, A., José, M., Machado, C., Márcia, Y., Pasa, D.: The effect of temperature on the properties of the NBR/PVC blend exposed to ethanolfuel and different gasolines. Fuel **113**, 679–689 (2013)

11. Ajanovic, A.: Biofuels versus food production: Does biofuels production increase food prices? *Energy* **36**, 2070–2076 (2011)
12. Bentivoglio, D., Rasetti, M.: Biofuel sustainability: review of implications for land use and food price. *Rivista di Economia Agraria*, Anno LXX, 7–31 (2015)
13. Popp, J., Lakner, Z., Harangi-Rákos, M., Fári, M.: The effect of bioenergy expansion: Food, energy, and environment. *Renew. Sustain. Energy Rev.* **32**, 559–578 (2014)
14. SSTU 8696:2016 Alternative fuels for gasoline engines. Specifications. Kyiv, Ukraine (2017)
15. Kuts, Yu., Povstyanoy, O.: Computer-informative software for research of the new materials of constructional application. *Funct. Mat.* **1**, 175–178 (2017)
16. Topilnytskyi, P., Hrynyshyn, O., Machynskyi, O.: Technology of Primary Processing of Oil and Gas: Textbook. Publisher of Lviv Polytechnic, Lviv (2014). (in Ukrainian)
17. Boichenko, S., Pushak, A., Topilnytskyi, P., Leida, K.: Motor fuels: properties and quality. Center for Educational Literature, Kyiv (2017)
18. SSTU 7687:2015 Gasoline car EURO. Technical conditions. Kyiv, Ukraine (2015)
19. Kozak, F., Melnyk, V., Prynko, I., Voitsechivska, T.: Economic efficiency of bioethanol use in internal combustion engines. *Automobile transport* **42**, 22–28 (2018)
20. Makarov, V., Petrykin, A., Emelianov, V., Shamonina, A., Varannik, V., Onoichenko, S.: Alcohols as additives to gasoline. *Automotive industry* **8**, 24 (2005)
21. Matiushyna, R., Achmetov, S., Shiryazdanov, R., Davletshin, A., Telyashev, E., Rachimov, M.: Priorities in the production and application of biofuels at the post-oil stage of fuel energy development. *Oil Refin. Petrochem.* **10**, 35–38 (2012)
22. Machiela, P.: Summary of the Fire Safety Impacts of Methanol as a Transportation Fuel (2001)
23. Varfolomeev, S., Efremenko, E., Krylova, L.: Biofuel. *Rus. Chem. Rev.* **79**(6), 491–509 (2010). <https://doi.org/10.1070/RC2010v079n06ABEH004138>
24. Bohdanov, S., Lavrik, A., Terevov, A.: Influence of oxygenate additives on anti-knock properties of fuels for automobile engines with forced ignition. *Bull. South Ural State Univ.* **23**, 86–89 (2008)
25. Onoichenko, C., Emelianov, V., Aleksandrova, E.: The use of additives based on isopropanol in the production of gasoline. *Oil Refin. Petrochem.* **2**, 32–36 (2003)
26. Tsarev, A., Karpov, S.: Increase of ecological and operational characteristics of automobile gasoline by introduction of oxygenates. *Chem. Technol.* **8**, 324–328 (2007)
27. Yakovlev, A., Melnichenko, I., Baklaeva, N., Ivanova, A.: Efficiency of application of ethyl-tert-butyl ether (ETBE) in the production of high-octane gasoline. Economics of oil refining (2009). <http://www.epn-consulting.ru/effektivnosti-primeneniya-etil-tret-butilovogo-efira-etbe-v-proizvodstve-vysokooktanovyx-avtobenzinov/>. Accessed 28 Oct 2019
28. Vildanov, F., Latypova, F., Chanyshiev, R., Daminev, R., Karimov, O., Mamlieva, A.: Production of ethyl tert butyl ether-a promising direction for the use of bioethanol in Russia. *Bashkir Chem. J.* **20**, 145–149 (2013)





# Improvement of the Production Technology of Liquid Biofuel from Technical Fats and Oils

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**Abstract.** Because of petrol energy saving, emission standards of diesel exhaust gases hazardous substances requirement toughening, as well as carbonic oxide exhaust emission control, many countries need to find how to reduce the negative influence of heat engine over the environment. The most important operation of biodiesel technical processing from fat and oil waste were studied. The importance of keeping within the mass ratio of fat, oil, and alcohol was shown. The influence of fat and oil quality stock raw materials on the composition of biodiesel were estimated. Requirements for input raw materials were developed. A determining influence of raw material moisture on the mechanism of triglycerides transesterification in fatty acids methyl ester was shown, that, according to its operational characteristics, is close to petro-diesel fuel. The raw material free fatty acids (FFA) in conjunction with water make the process ineffective. As a result of scientific research, the technology of biodiesel production from vegetable oils and animal fats has been substantiated and its equipment support is offered. Experimental - industrial tests of mobile plants showed its possible to produce a good quality product that meets the modern operational requirements for biodiesel that could be used in engines without significant redesign. As a result of scientific research, the technology of biodiesel production from vegetable oils and animal fats has been substantiated and its equipment support was offered. A hardware-processing configuration and a layout equipment plant of mobile plant for the production of biodiesel from fats and oils were developed.

**Keywords:** Waste · Animal fat · Vegetable oil · Alcohols · Free fatty acids · Transesterification · Bio-Fuel · Plant

## 1 Introduction

Dependence on the petrol import of more countries places a premium one problem of national, economic and energy security, by contrast, overuse of petroleum products poses a significant environmental hazard. This particular cause determines the need for research and development aimed at diversifying the raw material base as well as search for alternative motor fuels for cars, mechanisms, and vehicles [1, 9].

Ukrainian meat processing factories have enough resources of animal fat and fatty waste, annually accumulate in volume about 200 thousand tons. There is a technical possibility of its utilization due to the processing of environmentally friendly fuel with a high-quality rate [1–4].

Synthesized alternative fuel from vegetable oils and industrial animal fats, agricultural and restaurants wastes, seaweeds, etc., also form carbon dioxide during burning, but this gas that was previously consumed by plants from the air, and because of this the use of biomass as a fuel raw materials reduces the greenhouse effect that disturbs the Earth population [1, 16].

## 2 Literature Review

A diesel engine inventor - Rudolf Diesel in 1900 during the worldwide exhibition in Paris demonstrated a diesel engine that worked on vegetable peanut butter [2]. It was not until later that, thanks to the low price of petroleum fuels it began to be used in diesel engines and, with its further improvement, focused on petroleum products [3].

Technical animal fats (TAF), waste edible oils, as raw material sources of energy, are not only an alternative to reducing the cost of fossil fuels in agricultural production and transport companies, it is as well an important factor in the environmentally friendly energy supply system [1].

Vegetable and animal oils and fats (VAOF) are the future-proof raw material for the industrial production of biodiesel, because biofuels, obtained as a result of their transesterification by alcohols, have the characteristics similar with those of fuel derived from petroleum. This fuel should be used for diesel engines even with no construction modification [1].

VAOF consists of triglycerides, free fatty acids, phospholipids, stearin and often of the excess of water. VAOF usually has a lot of dirt that gives a special property for this raw material and prevents its direct consumption not only for food purposes but also for fuel production [4]. These problems could be eliminated by purification and some transformation of the chemical composition of fats and its subsequent alcohol exchange [3].

Methanol, ethanol, propanol, butanol and other alcohols can be used to fat triglycerides transesterification, and its monoesters are correspondingly called methyl, ethyl, propyl, and butyl esters. Methyl alcohol is the most commonly used [4].

The production of biofuels from fatty raw materials would reduce its cost and allowed making the best use of fat waste, as well as have a positive influence on environmental conditions in Ukrainian localities and reduce the negative motor vehicle emissions impact on the public health [5].

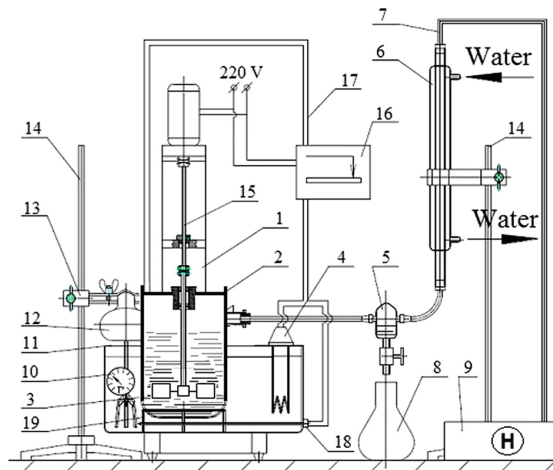
Consequently, trending is the search for alternative, cheaper and more environmentally friendly fuels that are meant to be biodiesel based on lipids, which could be produced directly by agricultural enterprises and the meat and dairy industries' enterprises. Increasing the VAOF's processing efficiency and production of biodiesel is an actual research issue [1].

The goal of research. Traditional industrial biodiesel processing design includes preliminary mechanical purification of raw materials (oils or fats), neutralization of its free fatty acids, that complicate processing and increase its time [6]. It's various well

known technological improvements of fatty acid esters production that improve the quality of the fuel but do not allow increasing its yield and reducing the reaction time [7]. Consequently, the improved production technology biodiesel and corresponding equipment, in particular for waste fats and oils, is a strategic technical pathway that requires a scientific and practical study, and that is the goal of the presented research.

### 3 Research Methodology

Experimental studies were conducted to assess the influence of the main parameters of the process of conversion of animal fats and vegetable oils to methanol with a catalyst KOH on the quantity and quality of methyl esters of fatty acids. To carry out the research, a developed and manufactured laboratory plant was used (see Fig. 1) [1].



**Fig. 1.** Laboratory installation for biofuel research [1]: 1 – engine tripod; 2 – vial for reagent; 3 – mixer; 4 – thermostat; 5 – condensate collection; 6 – refrigerator; 7 – pipeline; 8 – flask for collecting condensate; 9 – vacuum pump; 10 – thermometer; 11 – “water bath”; 12 – capacity for the preparation of potassium methylate; 13 – clamp; 14 – tripod; 15 – shaft mixer; 16 – thermoregulatory; 18 – thermocouple installed in the body of the “water bath”; 19 – stand.

IT allows changing according to the plan of the full factor experiment of type  $2^4$  of the reagent composition, to regulate the speed of the mixer shaft and the temperature of the technological process. Experiments were carried out using oils and fats with an acid number of 2–5 mg KOH/g. The frequency of rotation of the shaft of the mixer varied from 10.5 to 52.4  $s^{-1}$  at an interval of 10.5  $s^{-1}$ ; the temperature was maintained by the liquid thermostat TZh-TS-01/12 in the range from 20 °C to 70 °C in a step of 10 °C [1].

In the pilot studies, the following indicators of biodiesel quality were determined: density - with the help of pycnometers; viscosity – viscosimeter of the VLZ - 1 with a diameter of the capillary 0,54 mm; flash temperature in a closed crucible - device

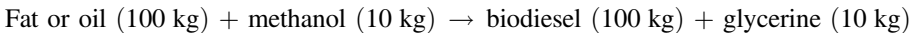
TVZ-LAB-01; acid number - titration of free fatty acids with aqueous KOH solution. Quantitative characteristics of the process of transesterification (volume of ether and glyceride phases) are established using measuring cylinders [1].

In the course of experimental studies, the effect of reagent concentration, temperature, design parameters of periodic and continuous reactors and mechanisms of mixing mechanization on the technological parameters of the process of transformation of fats into biodiesel was established [1, 6].

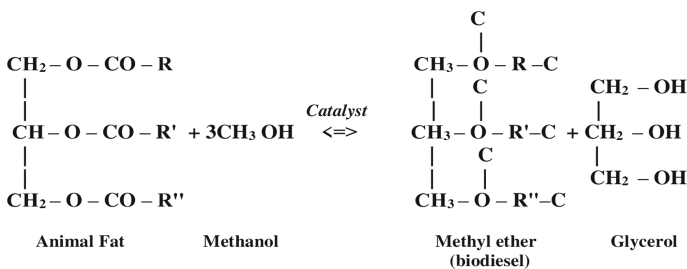
In the study of biodiesel production, methods of experimental-statistical simulation using the software package Mathcad 15 were used. To do this, the experiment plan 24 was used with interdependent variables. The assessment of the quality of biodiesel was carried out in accordance with DSTU 6081: 2009 and EN 14214: 2003 [13, 14].

Biodiesel can be produced from any vegetable oil or animal fat through the fatty acids esterification method. Of course, in its chemical nature, fats, for example, have a vegetable origin – it is a composition of esters of triatomic alcohol (glycerine) and many fatty acids [1, 8, 20]. Glycerine in fats can be substituted by molecules of methyl or ethyl alcohol and as well get ether, but with a lower pour point temperature and a smaller viscosity. These fatty acids methyl (ethyl) esters (esters) are exactly biodiesel. The main co-product of the reaction of oil transesterification is glycerol with some dirt. Such kind of glycerol after purification should be used in the chemical, pharmaceutical and perfumery industries.

Even a tenuous review of literature sources shows that in obtaining diesel biofuel, for example, from vegetable oils, the valid approximate ratio is the following [9, 10]:



This ratio is a simplified formula for the following reaction of the transesterification of triglycerides (see Fig. 2).

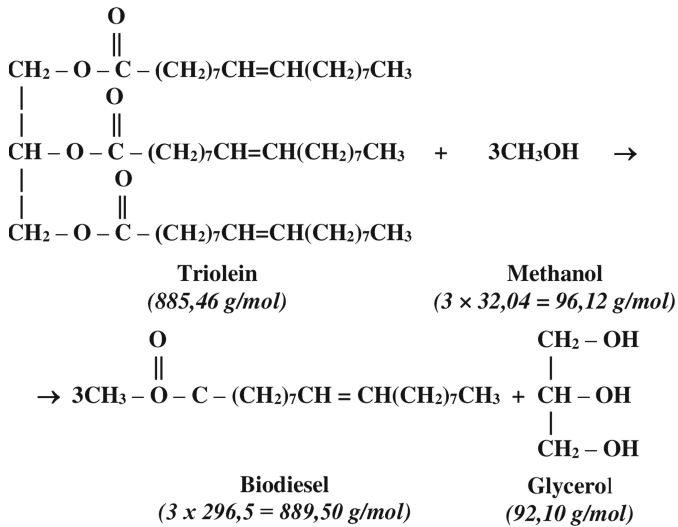


**Fig. 2.** Simplified formula for the reaction of the transesterification of triglycerides R, R', R'' – is a long chain of carbon and hydrogen atoms, called chain fatty acids. For example, palmitinic acid form chain R = – (CH<sub>2</sub>)<sub>14</sub> – CH<sub>3</sub>, stearinic acid - R = – (CH<sub>2</sub>)<sub>16</sub> – CH<sub>3</sub>, oleinic acid - R = – (CH<sub>2</sub>)<sub>7</sub>CH = CH(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>, linolic acid - R = – (CH<sub>2</sub>)<sub>7</sub>CH = CH – CH<sub>2</sub> – CH = CH(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, linolenic acid - R = – (CH<sub>2</sub>)<sub>7</sub>CH = CH – CH<sub>2</sub> – CH = CH – CH<sub>2</sub> – CH.

These five types of chains are oils and animal fats distinguishing that make possible production of diesel biofuel.

For clarity, we consider oils and animal fats and assume that its triglyceride consists of three acid chains of only oleinic acid.

Reacting with methanol over the KOH catalyst, such a triglyceride would yield the following resultant (see Fig. 3).



**Fig. 3.** Scheme of the reaction of transesterification of fats using methanol and potassium hydroxide.

The molecular mass of triolein is 889.50 g/mol, and the biodiesel fuel extracted from triolein is 885.46 g/mol.

Giving a 100% excess of methanol would ensure a reaction guaranteed to undergo. Then the reaction mass balance could be written the following way:

$$\begin{array}{l}
 \text{Fat or oil (100 kg) + methanol (21, 71 kg)} \\
 \rightarrow \text{biodiesel (100, 45 kg) + methanol (10, 86 kg)}
 \end{array} \tag{1}$$

For the reaction undergoing, 1% weight part of catalyst KOH comparing to oil mass is required. This mass balance can be compared to the volume of the reagent. Then the specific gravity of the reagents in the reaction (kg/l) would be distributed the following way: triolein - 0,8988; methanol - 0,7914; biodiesel - 0,8739; glycerine - 1,263.

## 4 Results

According to the results of laboratory tests, the obtained biodiesel was found to meet the Biofuel Standards for Transport in the EU EN 14214:2003 assumes 0,24% of glycerine in the fuel. In the case that the triglycerides compose exclusively of trioleines, the glycerine molecule would weigh 92.10 g/mol, and the triolein molecule would weigh 885.46 g/mol. Thus, trioleine contains  $92.10/885.46 = 0.104$ , or 10.4% glycerine. This glycerine is fixed because of attachment to the triglyceride molecule. If the oil contains 10.4% of glycerine to prevent its conversion to monoglycerides and diglycerides, upon condition that biodiesel contains 0.24% of glycerol, the reaction of the transesterification of the triglyceride should be 97.7% chemical reaction:

$$\frac{10,4 - 0,24}{10,4} \cdot 100 = 97,7\% \quad (2)$$

This can not always be done, especially when the oil has excess water and free fatty acids that are present as well, usually in crude oils.

For example, free oleinic acid interacting with a catalyst over water forms soap and the catalyst bind in forms that do not accelerate the reaction of transesterification and do not facilitate the separation of glycerine from triglycerides.

Because of this, free fatty acids and water should be present in oils in at the minimum [11, 18, 20, 22].

If the water in the oil is present in a significant amount, then in conditions of higher-temperature there could be no reaction of the transesterification, but the reaction of hydrolysis of triglycerides in diglycerides and free fatty acid [1, 17–20].

Free fatty acids over a KOH catalyst could further be converted into a quantity of soap that binds gel reagents. It would not divide into biofuel and glycerol after the reaction completion.

As a rule, for the production of biodiesel from the existing range of alcohols, methanol would be selected (R correspond to CH<sub>3</sub>), but it is possible to use other alcohols, such as ethanol. To ensure that the reaction would proceed from left to right in the arrow direction, it should add an excess of methanol in the reactor, and reaction could be carried out properly at optimal pressure and temperature over an optimal catalyst amount, that is practically a know-how.

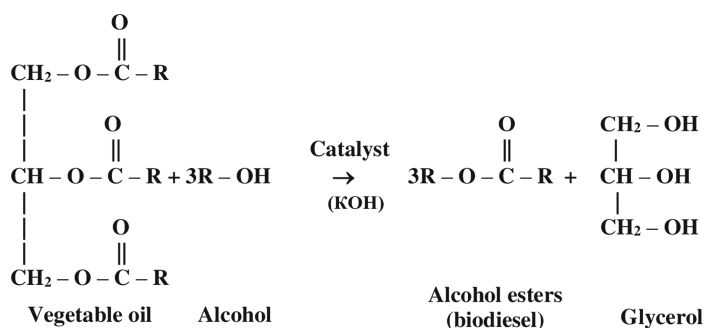
After conducting experimental studies, it was found that the biodiesel fuel production from fat or oil must undergo an irreversible reaction, in general terms, it could be written as (Fig. 4).

Thus, the final quality of diesel fuel depends on the following: the amount of water in the raw material, its impurity of free fatty acids, the quality of methyl alcohol, the amount of catalyst, the temperature and pressure in the reactor, the presence of a biofuels washing operation, the period of the transesterification process, the availability of a fuel purification system from foreign inclusions, etc.

Besides triglycerides in a reagent, the mixture could be monoglycerides, excess methanol, glycerol, the catalyst that contaminate the final product. Therefore, after demixing and fractionation of reagents mixture, the raw biodiesel should be rinsed well with water with often added small amounts of sulphuric acid or edible salt. And at the

final stage of fuel production, methanol and water should be removed (“dry”) in rectification tower with a special nozzle [1, 16].

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**Fig. 4.** Scheme of the irreversible reaction of biodiesel production from vegetable and animal fats.

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A number of technological process parameters are practically very difficult to calculate, because of this we have identified such parameters experimentally and it would compose the issue of the next publication.

All the calculations and researches made it possible to develop the equipment and technological scheme of the line for the production of diesel biofuels from food and processing wastes and to design the technology of biofuels production (see Fig. 5).

The process of production of diesel biofuels consists of several stages, which are implemented in the oil - purification and ester modules of the plant.

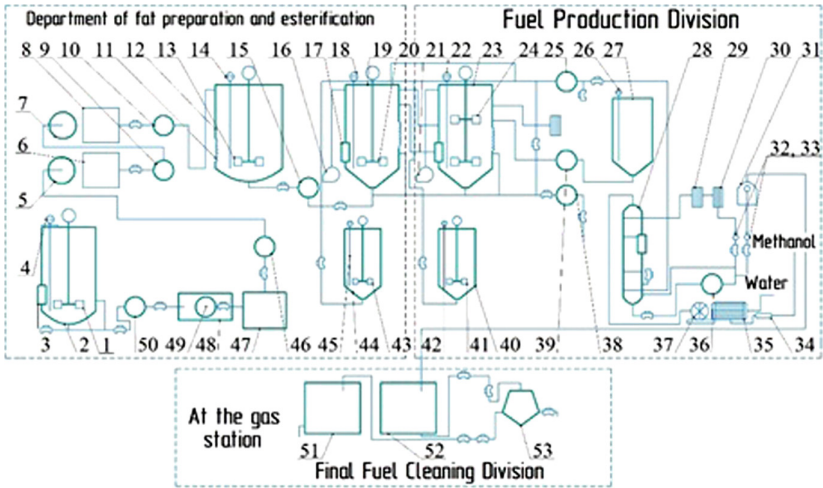
Pre-purified and heated to the temperature of the transesterification reaction fat is fed into the reactor.

The apparatus 40 pre-prepares an alcohol-catalytic solution (for example, methyl alcohol and caustic potassium), which is fed into the reactor 23. Under constant stirring and heating in the reactor, the formation of esters.

Upon completion of the transesterification reaction and settling of the reaction mixture from the reactor 23, the pump removes glycerol (crude glycerol). The reactor is then fed a pre-prepared washing solution (acidic or neutral) from tank 27. This solution allows the pre-selection of soap, methanol, and surfactants from the precipitate, which

is removed from the reactor and sent for further treatment to be removed from the reactor. It has some useful fractions used for the preparation of detergents and lubricants for metalworking.

The obtained esters from the reactor, using pumps, are fed to a rotary distillation unit 28 where the reaction products are separated into esters, water, and methyl vapors and by-products. Methanol and water vapors are condensed in the absorber 36. The recovered methanol is returned to the apparatus 40 and the water to special storage.



**Fig. 5.** Technological scheme of the line for biodiesel production from food and processing wastes.

The pre-purified water and methanol fatty esters, after passing through a system of filters 31 filled with the adsorbent “Amberlite”, are further purified from water, glycerol, soap and fall into the collecting tank. Pure esters are collected into a container 51 and then pumped into a refueling column. Due to the preliminary purification of raw materials and the correction of fatty acidity, the use of a rotary distillation unit 28 and a vacuum pump 37 (Fig. 5), the filter system 31 with the adsorbent “Amberlite” and the separator 53 managed to obtain diesel fuel, which is of European quality (EN 14214) and national (DSTU 6081: 2009) [1, 11, 12] standards.

Such technology of production of biodiesel from technical animal fats can be implemented at the mobile plant located on two metal platforms with a size of  $12000 \times 2400$  mm, which are easily transported on car trailers - long-distance.

It should be noted that to ensure the biofuels required quality, it is necessary to set strict requirements for raw materials.

The designed technological process and manufactured automatic mobile plants for the production of biodiesel are exploited at OJSC “Proskuriv” (Khmelnysky city) and the Chyhyrnsky agrarian company, and the high quality of biological fuel is confirmed by the Ukrainian Research Institute of Forecasting and Testing of Equipment for



Agricultural Production named after Leonid Pogorilyi of Ministry of agrarian policy and food of Ukraine [1, 2, 15].

When technical animal fat or oil is used for the production of biodiesel, it must first be pre-processed:

- Melting;
- Separation of the melted fat-water-protein mixture by centrifugation on a solid precipitate and a fat-water emulsion;
- Separation of a fat-water emulsion to get free-of-liquid fat;
- Bringing the acid index to the norm.

The innovative technical solutions, used in the processing configuration, allowed to provide production of high-quality biofuels. Thus, the kinematic viscosity of fuel at a temperature of 40 °C is 4.5 mm<sup>2</sup>/s, that meets the requirements of current standards (3.5, ..., 5.0 mm<sup>2</sup>/s), the flashpoint is 140 °C (for the euro standard, not less than 120 °C), that positively affects the operation of diesel engines. The fuel density at a temperature of 15 °C is 880 kg/m<sup>3</sup>, which is also within the norm. Methanol, water, sulfur, glycerin, mechanical dirt and soap residues in fuel are completely absent, and therefore it could be considered environmentally friendly and safe to use. The cetane number is 53 (at least 51), that ensures effective combustion in the engine, and the acid value does not exceed 0.15 mg KOH/g (by standard no more than 0.5).

## 5 Conclusions

To ensure the biodiesel meets requirements of the existing standards, special attention must be paid to the preparation of raw materials for processing, notably: to ensure the moisture content in fatty substances is not higher than 7%, to reduce the acid value to 2 mg KOH/g due to neutralization of free fatty acids, as well as remove mechanical dirt and use pure methanol (99.8%) and water with a neutral reaction for washing biofuels.

A strong effect on the quality of fuel exercise the temperature and pressure in the reactor, the amount of catalyst, the duration of the transesterification process, the presence in the processing fuel washing and drying.

Experimental - industrial tests of mobile plants showed its possible to produce a good quality product that meets the modern operational requirements for biodiesel that could be used in engines without significant redesign.

The quality of diesel biofuel, manufactured by the implemented mobile plants meets the requirements of DSTU 6081:2009 and EN 14214:2003.

The results of research into the conversion of fat waste into biodiesel in the future will be the basis for the design of technological equipment and optimization of its modes of operation, as this area is a relevant topic of research.







## References

1. Mushtruk, M., Sukhenko, Yu., Boyko, Yu.: Deep Processing of Fats in Bioproducts. Comprint, Kyiv (2017)

2. Farooq, M., Ramli, A., Subbarao, D.: Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts. *J. Clean. Prod.* **59**, 131–140 (2013)
3. Adewale, P., Dumont, M., Ngadi, M.: Recent trends of biodiesel production from animal fat wastes and associated production techniques. *Renew. Sustain. Energy Rev.* **45**, 574–588 (2015)
4. Banković-Ilić, I., Stojković, I., Stamenković, O., et al.: Waste animal fats as feedstocks for biodiesel production. *Renew. Sustain. Energy Rev.* **32**, 238–254 (2014)
5. Sukhenko, Yu., Sukhenko, V., Mushtruk, M., et al.: Changing the quality of ground meat for sausage products in the process of grinding. *East. Eur. J. Enterp. Technol.* **4**(11(88)), 56–63 (2017)
6. Barnwal, K.: Prospects of biodiesel production from vegetable oils in India. *Renew. Sustain. Energy Rev.* **9**(4), 363–378 (2015)
7. Sukhenko, Y., Sukhenko, V., Mushtruk, M., Litvinenko, A.: Mathematical model of corrosive-mechanic wear materials in technological medium of food industry. In: Ivanov, V., et al. (eds.) *DSMIE-2018. LNME*, pp. 507–514. Springer, Cham (2019)
8. Nisar, J.: Enhanced biodiesel production from *Jatropha* oil using calcined waste animal bones as catalyst. *Renew. Energy* **101**, 111–119 (2017)
9. Sander, A., Koščak, M., Kosir, D., Milosavljević, N.: The influence of animal fat type and purification conditions on biodiesel quality. *Renew. Energy* **118**, 752–760 (2018)
10. Kirubakaran, M., Selvan, V.: A comprehensive review of low cost biodiesel production from waste chicken fat. *Renew. Sustain. Energy Rev.* **82**, 390–401 (2018)
11. DSTU 6081:2009.: Documentation – Presentation of these and similar documents
12. EN 14214:2003.: Documentation – Presentation of these and similar documents
13. Xiong, H., Guo, X., Xie, W.: Biodiesel remote monitoring system design based on IOT. In: *LNCS*, pp. 750–756 (2018)
14. Chai, M., Tu, Q., Lu, M.: Etherification pretreatment of free fatty acid in biodiesel production, from laboratory to industry. *Fuel Process. Technol.* **125**, 106–113 (2014)
15. Hawrot, M., Wijatkowski, A., Mikiciuk, M.: Influence of diesel and biodiesel fuel–contaminated soil on microorganisms, growth and development of plants. *Plant Soil Environ.* **60**(35), 189–194 (2015)
16. Issariyakul, T., Dalai, A.: Biodiesel from vegetable oils. *Renew. Sustain. Energy Rev.* **31**, 446–471 (2014)
17. Nielsen, P., Rancke-Madsen, A., Holm, H.: Production of biodiesel using liquid lipase formulations. *J. Am. Oil Chem. Soc.* **93**(7), 905–910 (2016)
18. Surendra, K., Olivier, R., Tomberlin, J., et al.: Bioconversion of organic wastes into biodiesel and animal feed via insect farming. *Renewable Energy* **98**, 197–202 (2016)
19. Sheiko, T., Tkachenko, S., Mushtruk, M., et al.: The studying the processing of food dye from beet juice. *Potravinarstvo Slovak J. Food Sci.* **13**(1), 688–694 (2019)
20. Mohadesi, M., Aghel, B., Maleki, M., Ansari, A.: Production of biodiesel from waste cooking oil using a homogeneous catalyst: Study of semi–industrial pilot of micro reactor. *Renew. Energy* **136**, 677–682 (2019)
21. Bentivoglio, D., Rasetti, M.: Biofuel sustainability: review of implications for land use and food price. *Rivista di Economia Agraria Anno LXX*, 7–31 (2015)
22. Pinzi, S., Leiva, D., López-García, I., et al.: Latest trends in feed stocks for biodiesel production. *Biofuels, Bioprod. Biorefin.* **8**(1), 126–143 (2014)
23. Mohammadshirazi, A., Akram, A., Rafiee, S., et al.: Energy and cost analyses of biodiesel production from waste cooking oil. *Renew. Sustain. Energy Rev.* **33**, 44–49 (2014)



# Influence of the Magnetic Field Gradient on the Efficiency of Magnetic Water Treatment

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**Abstract.** This paper focuses on the study of the influence of a magnetic field gradient on the efficiency of the magnetic water treatment process (MWT). For this purpose, the changes in the kinetics of oxidation of organic matter with ozone were used. The methods of theoretical analysis of the geometry of the magnetic field in the equipment of water purification technologies were applied for experimental study of the influence of the inhomogeneous magnetic field on the kinetics of the oxidation reaction of organic pollution. Statistical processing of experimental results allowed approximation of the regression equation of MWT efficiency on the rate of magnetic induction change and duration of processing. The efficiency of MWT does not increase monotonically with increasing duration of the MWT process both increasing the value of magnetic induction change. The speed of the aqueous solution and the geometry of the inhomogeneous magnetic field are closely related and have been one of the main parameters that determine the MWT efficiency. These parameters can be expressed by the magnitude of the magnetic induction change. Experimentally established dependencies can find application in the development of scientific and methodological bases for the implementation of the process of magnetic treatment of polluted waters for the purification intensification in environmental protection systems.

**Keywords:** Magnetic water treatment · Aqueous solution · Inhomogeneous magnetic field · Magnetic induction change · Magnitude

## 1 Introduction

The current situation is alarming regarding great water scarcity, even in water-rich regions. It requires innovative technologies to ensure proper treatment of raw, process, and sewage waters. To solve this problem, we need to identify robust methods of purifying water at a lower cost and with less energy. At the same time, we should minimize the anthropogenic impact on the environment. Magnetic water treatment (MWT) is one of such perspective methods. This technology is not a new one, but it remains relevant.

Changes in the physicochemical properties of aqueous solutions (such as kinetics of reactions, hydration of solutes, density, viscosity and surface tension of an aqueous solution) are the basic principles of water treatment using magnetic fields. The main parameters of MWT are magnetic field characteristics. The sizes of the device and magnets themselves, their location, depend on them. These are the basic contour and mode parameters of the magnetic treatment devices. The obtained results find practical application in water treatment processes and allow choosing the optimum design and mode processing parameters.

## 2 Literature Review

Magnetic treatment is used with different propose for many processes. The use of magnetic processing can be widely used in environmental protection. In addition to water treatment [1], it is promising regarding leaching some ions from the soil [2].

The main problem of the magnetic water treatment implementation is the lack of studies of the mechanisms of the MWT effect. The magnetic field has an influence on chemical properties of water, scale formation and morphology [3]. It can modify the detergency and the mineral fouling [4] and the accelerated coagulation of scale-forming particles [5]. However, most studies are focused on the effect of reducing carbonate deposit during MWT application [6–9]. This fact confirms the lack of knowledge regarding the dependence efficiency of the magnetic processing on the characteristics of the magnetic field.

The results of different studies [5, 10, 11] and the practical experience of applying MWT prove that the effects of MWT have a complex dependence on MWT parameters and do not increase in proportion with the magnetic induction. The variety of MWT data, their incomprehensibility, volatility, and practical relevance have led to the emergence of different hypotheses for the MWT mechanism [12].

The lack of common approaches to the interpretation of the nature of physical and chemical effects of MWT, general principles of the process, and the criteria for selecting the optimal design parameters of MWT devices, led to the emergence of a large variety of MWT devices. They differ in several features (Fig. 1 - author's classification). MWT devices differ by the type and shape of magnets, the completeness of the magnetic field use, the scope, conditions of use and design features, etc.

The basis of all types of MWT devices is the motion of an aqueous solution in a non-uniform magnetic field (the presence of the apparatus sections with a magnetic induction drop  $\Delta V \neq 0$ ). The geometry of the magnetic field and the inhomogeneity of the magnetic induction distribution along the pipe while passing aqueous solution are the most significant parameters. It depends on the characteristics of the magnets (polarity, magnetization method, pole shape) and their arrangement along the water trajectory [13, 14]. MWT efficiency is also influenced by the duration of treatment and physical parameters of water (temperature), mineral and dispersed composition [15–18].

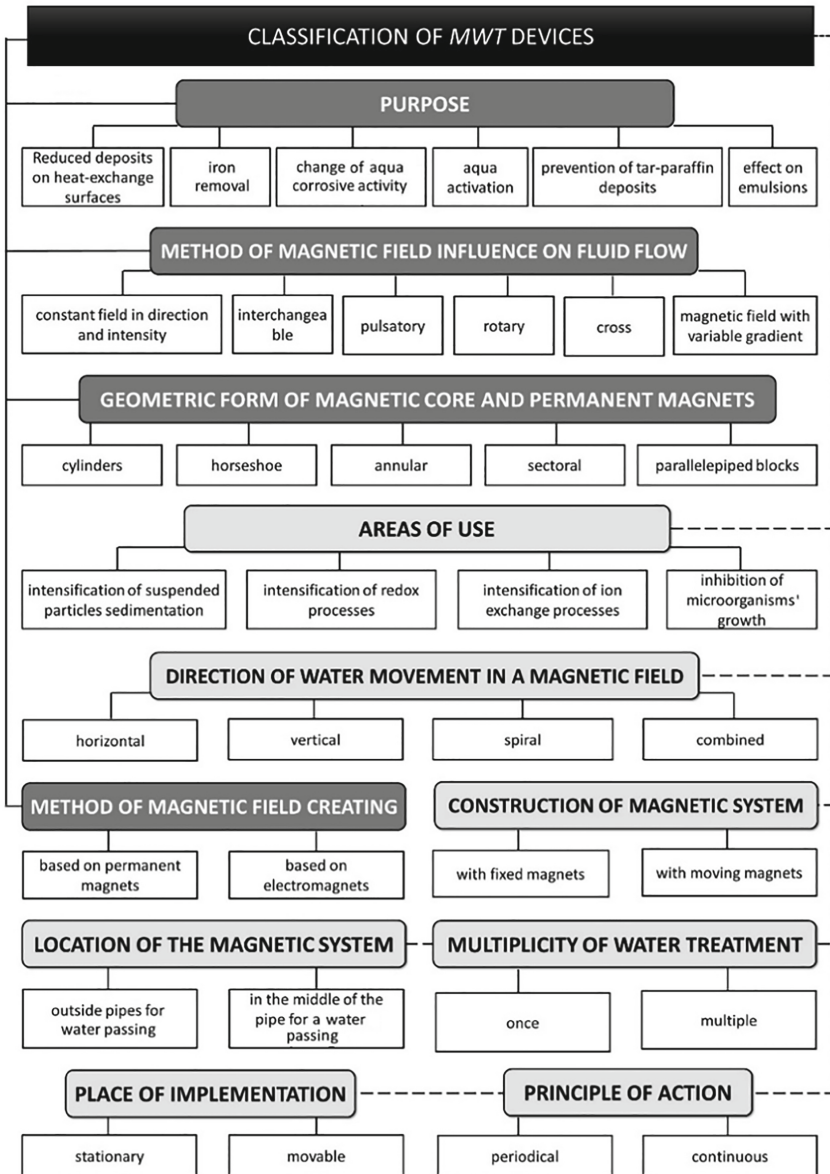


Fig. 1. Classification of MWT devices.

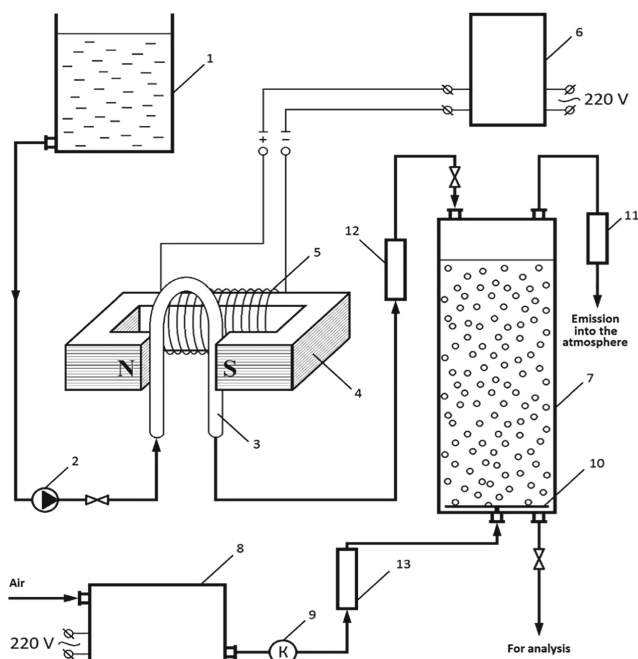
The gradient of the magnetic field is a more important factor than the magnetic field strength [19]. This effect was experimentally confirmed. New approaches have been proposed by [15] to explain the increased rate of water evaporation using a magnetic field.

One of the indicators of an inhomogeneous magnetic field impact on an aqueous solution and the course of subsequent processes is a change in the kinetics of chemical reactions. So, the main aim of this research is to carry out experimental studies of MWT parameters impact on the reaction kinetics of organic matter oxidation with ozone. Ozone was chosen as an indicator of changes in the physicochemical properties of an aqueous solution after MWT.

### 3 Research Methodology

Experimental studies of the directional influence of an inhomogeneous magnetic field on the oxidation kinetics of organic compounds with ozone were carried out using an oxalic acid solution. It is relatively slow oxidized by ozone, which made it possible to monitor the effectiveness of MWT. MWT efficiency was defined as an increase in the efficiency of oxidization of oxalic acid (%) relative to the usual conditions of oxidation.

For the experimental studies a laboratory stand was made (see Fig. 2).



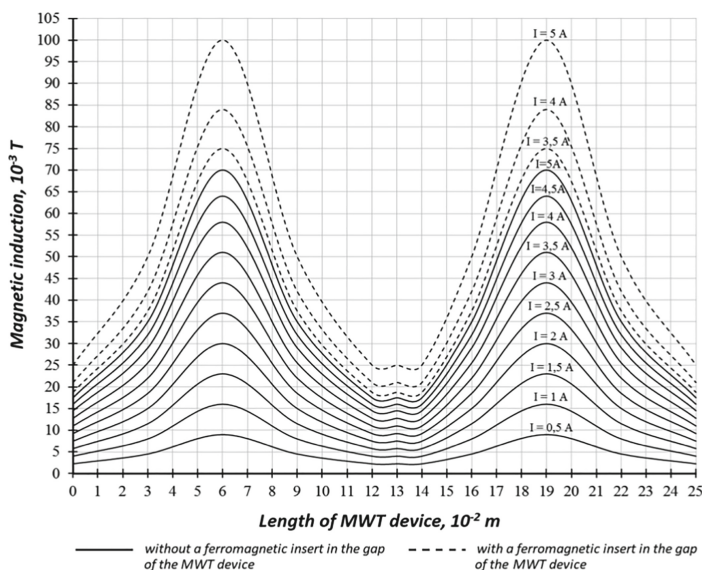
**Fig. 2.** Laboratory stand for studying the influence of MWT on the kinetics of oxidation reaction; 1 – tank with the working solution; 2 – pump; 3 – pipe for passing the solution in the gap between the poles of the magnets; 4 – from electrical steel core; 5 – coil; 6 – AC rectifier; 7 – bubbling reactor; 8 – ozonator; 9 – air compressor; 10 – dispersing element; 11 – activated carbon column.

The working solution (with a given concentration of oxalic acid and pH) from the tank (1) using the pump (2) was fed into a pipe (3). The pipe is made of diamagnetic material and placed in the gap of electrical steel core (4), on which the coil (5) is wound. At the same time, when passing the solution through the pipe (3), the coil (5) was fed a direct current from the rectifier (6). When passing DC through the coil (5) in the core gap (4) there is a magnetic field, the induction of which depends on the amount of direct current, which allowed regulating the magnitude of the magnetic field induction in the gap of the apparatus of magnetic processing. The magnetic field treated solution from the pipe (3), which then was fed into the bubbling reactor (7).

After filling the reactor (7) from the ozonator (8) using the compressor (9), the ozone-air mixture was fed into the reactor (7) through the dispersing element (10). The dispersing element is a ceramic plate. The ozone-air mixture, which passed the solution, was fed into the column (11) through the pipe outlet. Then the air mixture purified of ozone went to the atmosphere.

To study the influence of the regime parameters of the MWT devices, a series of experiments were carried out according to a similar process scheme - a single passage of a solution in a magnetic field and further ozonation. The effect of each of the defined mode parameters was studied independently.

The studies used experimental solutions with a constant concentration of oxalic acid ( $C_2H_2O_4$ ) –  $0.1 \text{ kg/m}^3$ . The initial pH level was taken as 7. The solution temperature was  $293 \text{ K} (\pm 0,2)$ . Further ozonation of solutions for all experiments was carried out under similar conditions with a constant flow rate of the ozone-air mixture of  $1.67 \cdot 10^{-6} \text{ m}^3/\text{s}$  and ozone concentration –  $0.16 \text{ kg/m}^3$ . Ozonation in a bubbling reactor was carried out during 1200 s.



**Fig. 3.** The change in the magnetic induction in the gap of the MWT device along the tube for aqueous solution passing.

The inhomogeneity of the magnetic field in the MWT device in regard to the unit volume of the solution was provided by the movement of the aqueous solution in the magnetic field with the magnitude variation from 0 to  $B_i$ , along the trajectory. The differential induction of  $\Delta B$  was ensured by the non-uniformity of its distribution along the pipe for aqueous solution passage (Fig. 3) At a constant length of pipe section  $l_i$ , the inhomogeneity of the magnetic field was ensured by a change in magnetic induction, from 0 to  $B_i$ , or  $B'_i$ , which allowed the inhomogeneity change of the magnetic field at other constant processing parameters.

Theoretical aspects of the work are based on physical and mathematical modeling. The methods of titrimetric analysis and pH-metry were used to determine the efficiency of organic matter oxidation and control of the physicochemical parameters of MWT and ozonation processes. The experimental data were processed using regression analysis software packages.

## 4 Results

The long-term operation of MWT devices [11, 12, 15, 16] has proved that the obligatory condition of MWT is the movement of an aqueous solution in a non-uniform magnetic field. The speed of the aqueous solution is one of the determining parameters of MWT. The analysis of the typical frame showed that the principle of MWT devices is the movement of an aqueous solution with velocity  $v_S$  in a section of pipe with the length  $l$ , placed in a non-uniform magnetic field, where the magnetic induction varies from  $B_{min}$  to  $B_{max}$ , or vice versa. The analysis of the elementary area of any MWT device proves that at  $v_S = 0$  the magnetic field will be constant for each unit of water volume for any induction drop  $\Delta B$  in the section  $l$ . From a physical point of view, it is clear that the velocity  $v_S$  directly affects the magnitude of the magnetic induction drop  $\Delta B$  for a solution volume unit. But the maximum magnitude of the magnetic field induction  $B_{max}$  is not so important at the value  $\Delta B/\Delta t$ . It coincides with [16], where the effect of MWT is observed at low induction values.

The MWT efficiency depends on the processing time and the solution speed in an inhomogeneous magnetic field. Such dependencies are complicated by the design parameters of the MWT devices (placement of magnets, the length of the MWT devices sections with the magnetic induction drops). The influence of the rate of magnetic induction change  $v_B$  (T/s) on MWT efficiency was analyzed considering all these parameters. The parameter  $v_B$  simultaneously takes into account the design parameters of MWT devices, such as the magnetic induction drop  $\Delta B$ , the length of the devices section with a non-uniform magnetic field  $l$ , and one mode parameter - the speed of the aqueous solution  $v_S$  (Eq. 1):

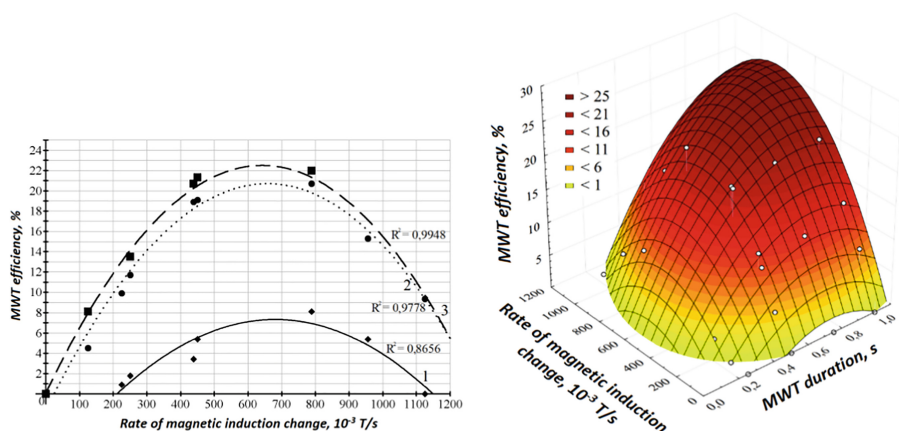
$$v_B = \frac{\Delta B}{\Delta t} = \frac{(B_{max} - B_{min})v_S}{l} \quad (1)$$

where  $B_{min}$ ,  $B_{max}$  – the minimum and maximum magnitudes of magnetic field induction at the pipe section where the magnetic induction changes, T;  $\Delta t$  – the time at which the aqueous solution passes the distance  $l$ , s;  $l$  – the length of the pipe section at which the



induction of the magnetic field changes from  $B_{min}$  to  $B_{max}$  or vice versa,  $m$ ;  $v_s$  - the speed of aqueous solution,  $m/s$ .

The dependence of MWT efficiency on the rate of magnetic induction changes ( $v_B$ ) with simultaneous consideration of the total duration of MWT ( $\tau$ ) was characterized by the largest increase in oxidation efficiency of oxalic acid with ozone (Fig. 4). The results of the control experiment were based on the oxidation of oxalic acid by ozone after passing the solution throughout the MWT device without switching on the magnetic field ( $v_B = 0$ ).



**Fig. 4.** Dependence of the MWT efficiency on the rate of magnetic induction change: points – experimental results; lines – mathematical modeling results 1 – MWT duration (0,25 s); 2 – MWT duration (0,5 s); 3 – MWT duration (1 s)

Statistical processing of experimental results allowed approximation of the regression equation of MWT efficiency on the rate of magnetic induction change  $v_B$  and duration of processing  $\tau$ :

$$E_{MWT} = -14,653 + 38,670v_B + 45,656\tau - 35,975v_B^2 - 30,851\tau^2 + 22,845v_B \cdot \tau,$$

where  $E_{MWT}$  – MWT efficiency, %;  $v_B$  – the rate of magnetic induction change, T/s;  $\tau$  – MWT duration, s.

The efficiency of MWT at a duration of 0.5–1 s, does not increase monotonically with increasing value of  $v_B$  and reaches its maximum in the range from  $400 \cdot 10^{-3}$  to  $800 \cdot 10^{-3}$  T/s. Increasing the rate of magnetic induction change above  $800 \cdot 10^{-3}$  T/17 s was carried out by creating a sharp drop in magnetic induction. The efficiency of MWT decreased due to higher magnitudes of magnetic induction even with other constant processing parameters. It indicates the complexity of the relationship between MWT efficiency and the magnitude of magnetic induction.

The efficiency of MWT does not increase monotonically with the increasing duration of the MWT process. Thus, at constant values of  $v_B$ , increased duration of

treatment from 0.25 to 0.5 s dramatically increases the oxidation efficiency of oxalic acid. At the processing time from 0.5 to 1 s oxidation efficiency does not increase significantly, and a further increase in the duration is technically unreasonable.

## 5 Conclusions

The speed of aqueous solution in an inhomogeneous magnetic field is determined by the conditions of the appearance of MWT effects, which are more than the magnitude of the induction of a magnetic field. The speed of the aqueous solution and the geometry of the inhomogeneous magnetic field are closely related and are one of the main parameters that determine the MWT efficiency. We can express these parameters using the magnitude of the magnetic induction change. It makes possible to explain the nature of the MWT effects on the processing of aqueous solutions by relatively weak magnetic fields.

The duration of the magnetic treatment has a significant effect on the intensity of MWT effects. The efficiency of MWT decreases while using higher magnitudes of magnetic induction. It indicates the complexity of the processes occurring in aqueous solutions under the influence of a non-uniform magnetic field and requires further studies.

Results will expand possibilities for using MWT in technological processes of water preparation and purification, such as scale deposition reduction on heat exchange surfaces, increasing the removal efficiency of suspended particles from contaminated water during the stages of coagulation, flotation or filtration. Increasing kinetics of chemical reactions after MWT reduces reagents' needs and increases the purification efficiency of reagent treatment of contaminated water.

## References

1. Zaidi, N.S., Sohaili, J., Muda, K., Sillanpää, M.: Magnetic field application and its potential in water and wastewater treatment systems. *Sep. Purif. Rev.* **43**(3), 206–240 (2013)
2. Zlotopolski, V.: The Impact of magnetic water treatment on salt distribution in a large unsaturated soil column. *Int. Soil Water Conserv. Res.* **5**(4), 253–257 (2017)
3. Latva, M., Inkinen, J., Rämöc, J., Kaunistoa, T., Mäkinena, R., Ahonen, M., Matilainen, J., Pehkonene, S.: Studies on the magnetic water treatment in new pilot scale drinking water system and in old existing real-life water system. *J. Water Proc. Eng.* **9**, 215–224 (2016)
4. Lipus, L.C., Ačko, B., Neral, B.: Influence of magnetic water treatment on fabrics' characteristics. *J. Clean. Prod.* **52**, 374–379 (2013)
5. Lipus, L.C., Kropob, J., Crepinseka, L.: Dispersion destabilization in magnetic water treatment. *J. Colloid Interface Sci.* **236**(1), 60–66 (2001)
6. Gryta, M.: The influence of magnetic water treatment on CaCO<sub>3</sub> scale formation in membrane distillation process. *Sep. Purif. Technol.* **80**(2), 293–299 (2011)
7. Mehta, D., Mazumdar, S., Singh, S.K.: Magnetic adsorbents for the treatment of water/wastewater – a review. *J. Water Process Eng.* **7**, 244–265 (2015)
8. Mahmoud, B., Yosra, M., Nadia, A.: Effects of magnetic treatment on scaling power of hard waters. *Sep. Purif. Technol.* **171**, 88–92 (2016)

9. Gilart, F., Deans, D., Ferrer, D., López, P., Ribeaux, G., Castillo, J.: High flow capacity devices for anti-scale magnetic treatment of water. *Chem. Eng. Process.* **70**, 211–216 (2013)
10. Kobe, S., Dražić, G., McGuinness, P.J., Stražičar, J.: The influence of the magnetic field on the crystallisation form of calcium carbonate and the testing of a magnetic water-treatment device. *J. Magn. Magn. Mater.* **236**(1–2), 71–76 (2001)
11. Toledo, E.J.L., Ramalho, T.C., Magriotis, Z.M.: Influence of magnetic field on physical–chemical properties of the liquid water: Insights from experimental and theoretical models. *J. Mol. Struct.* **888**, 409–415 (2008)
12. Plyatsuk, L.D., Roy, I.O., Chernysh, Y.Y., Kozii, I.S., Hurets, L.L., Musabekov, A.A.: Clarification of the recent scientific approaches in magnetic water treatment. *J. Eng. Sci.* **6** (1), F12–F18 (2019)
13. Seyfi, A., Afzalzadeh, R., Hajnorouzi, A.: Increase in water evaporation rate with increase in static magnetic field perpendicular to water–air interface. *Chem. Eng. Process.* **120**, 195–200 (2017)
14. Al-Ogaidi, A.A.M., Wayayok, A., Rowshon, M.K., Abdullah, A.F.: The influence of magnetized water on soil water dynamics under drip irrigation systems. *Agric. Water Manag.* **180**, 70–77 (2017)
15. Chibowski, E., Szcześ, A.: Magnetic water treatment – a review of the latest approaches. *Chemosphere* **203**, 54–67 (2018)
16. Koshoridze, S.I., Levin, Y.K.: Model of scale deposition with magnetic water treatment. Formerly *nanomech. Sci. Technol. Int. J.* **5**(1), 51–71 (2014)
17. Kozic, V., Hamler, A., Ban, I., Lipus, L.C.: Magnetic water treatment for scale control in heating and alkaline conditions. *Desalin. Water Treat.* **22**(1–3), 65–71 (2010)
18. Szcześ, A., Chibowski, E., Holysz, L., Rafalski, P.: Effects of static magnetic field on water at kinetic condition. *Chem. Eng. Process.* **50**(1), 124–127 (2011)
19. Coey, J.M.D.: Permanent magnets: plugging the gap. *Scr. Mater.* **67**(6), 524–529 (2012)



# Heat Exchange Characteristics of Trays for Concentrating Solutions in Direct Contact with Hot Gas Emissions

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**Abstract.** The paper presents the comparative study results of the thermal characteristics of trays applicable for concentrating technological and waste liquids in direct contact with hot gas emissions. The dual-flow tray with large perforation, a baffle tray, similar to that of the mixing condensers, and a paset, i.e. a tray, consisting of a funnel and a cone with a smaller outer diameter, mounted above it, were tested. The enthalpy exchange coefficient was chosen as a comparison parameter since it takes into account both “dry” (due to the temperature difference) and “wet” (due to evaporation) types of heat exchange. Using this coefficient, the degree of influence of liquid temperature and hydrodynamic factors (gas velocity and irrigation density) to the kinetics of enthalpy exchange during the interaction between air and 15% sodium chloride solution was evaluated. It was found out, that according to the degree of influence on the heat exchange intensity, factors arranged in the following sequence: air velocity, related to the entire apparatus cross-section; spray density and temperature.

Moreover, the impact of temperature appeared to be, although noticeable, but negligible. Processing the experimental results mathematically, formulas are obtained to calculate the enthalpy exchange coefficients for all contact trays researched. Recommendations are also provided for their use.

**Keywords:** Thermal characteristics · Dual-flow tray · Baffle tray · Paset · Direct contact heat exchanger · Enthalpy exchange coefficient

## 1 Introduction

The waste heat resources utilization is known to face some difficulties. First of all, it is their relatively low temperature, leading, to problems in finding consumers, on the one hand, and, on the other hand, to relatively high metal consumption and the cost of heat exchange equipment. Waste gas is usually contaminated with dust, and often with aggressive components. Also, hot wastewater often contains caustic substances, solid-phase and dissolved components that can deposit sediment on heat exchange surfaces.

Considering equipment, the so-called “contact heat utilizers”, in which hot gas in direct contact with the liquid heating and/or evaporating it, seem to be promising [1, 2]. The advantages of such equipment are simplicity, cheapness, high intensity of heat and

mass exchange processes, absence of a rigid surface that separates the heat exchange medium. The latter is especially important when the solution is highly corrosive or when solid sediment is observed. Anyway, the concentration of solutions in direct contact with flue gas cannot be concerned as the best method in terms of heat utilization. However, this disadvantage is relevant only if paid fuel is used to obtain the hot stream. When utilizing waste power resources, for example, flue gas, the level of heat use is minor in comparison with the mentioned advantages.

The purpose of this research is to find and compare the heat and mass exchange characteristics of trays proper to use in a heat exchange apparatus when working with both light liquid and suspensions, forming strong sediments.

## 2 Literature Review

### 2.1 Trays for Working with Waste Water

Most of the known contact heat exchangers are packed bed columns [1, 2], which are improper for working with suspensions and crystallizing liquids despite having appropriate heat and mass exchange characteristics. Therefore, only constructions of trays applicable to operate in apparatuses with step phase contact are considered below.

Apparatuses, sectionalized in height with dual-flow trays, which are disks perforated with holes from 60 to 120 mm in diameter, are of significant interest from the viewpoint of utilizing suspensions heat [3]. The study results of heat and mass exchange on these trays can be found in works [4]. Dual-flow trays are easy to manufacture and, as the experience of soda ash production has shown, they can work with deposits overgrown for a long time [3]. Nevertheless, their disadvantages are unstable hydrodynamic regime and insignificant transverse mixing [5]. The latter leads to liquid and gas bypass in case tray diameters are large [6].

Contact coolers with segment shelves (baffles tray) [7], similar in design to those used in mixing condensers, are widely used in the industry. Dusty gas can cool down without clogging inside the apparatus of this type. The baffle tray contact cooler is used for cooling coke gas, saturated with moisture from 80 to 35 °C. Such types of equipment are also used in soda ash production. In particular, data on the heat exchange properties of these apparatuses can be found in work [8].

To utilize the heat of the distillate liquid of soda ash production it is recommended in work [9] to use trays, formed by series cones and funnels overlapping 55–60% of the apparatus cross-section. In [9] this device is called a “cascading contact element.” Further for brevity, we will call it “paset”. As the researchers’ outline, the interphase surface on such trays is formed due to the distribution of the liquid by crushing it into separate streams and drops. This method is considered to be the best one for contact heat exchangers.

In direct contact apparatuses [10, 11] of various designs, the concentration process is accomplished both with direct-flow and with countercurrent flow of the liquid and the gas [12, 13].

In most studies of the heat and mass exchange characteristics in contact heat utilizing, the common problem mentioned is their relatively low accuracy. In the

calculations based on the equations obtained by the authors of these works, errors are no less than 15%. Using the water-air system as a model can also cause difficulties in implementing the results obtained to real industrial gas and liquid systems.

## 2.2 Calculation Methods for Contact Heat Exchangers

Engineering calculations of contact apparatuses are diversified. That represents the complexity of the hydrodynamic and thermal conditions in the active apparatus space to a certain extent, and, in particular, the difference in the formation methods of an interphase surface and its structure [14]. When studying the heat exchange characteristics of trays in direct liquid and gas contact, the peculiarity is in the close interdependence of heat and mass exchange (evaporation or condensation of liquid), which cannot be studied separately except special cases. Mathematical models, taking into account this feature by simultaneously calculating heat and mass exchange (see, for example, [15, 16]), are characterized by excessive complexity, which is not always offset by the corresponding accuracy.

Allowing both simple graphical and instrumental calculations, the methodological approach to the calculation of contact heat exchangers are considered to be of significant interest, presented in work [17]. Problems, noted above, can be overcome if heat and mass exchange processes are regarded as a single enthalpy exchange process. In this case, the driving force of the process is also calculated in units of specific enthalpy. It is believed that this approach was initially proposed by Merkel and Hirsch to calculate the first stage of the drying process. In work [18], it was adapted to calculate the processes of contact heat exchange of liquid and gas. Following the approach proposed in this work, the enthalpy of gas changes in contact with the liquid, both due to the evaporation of air (the so-called “wet” heat exchange) and due to heat exchange under different temperature (the so-called “dry” heat exchange), and it is proportional to the difference between the enthalpy of gas which is in equilibrium with liquid and the actual one. Mathematically, this can be given as follows:

$$G \frac{dH_g}{dS} = k_H (H_g - H^*). \quad (1)$$

$k_H$  is found by the formula:

$$\frac{1}{k_H} = \frac{1}{k_g} + \frac{H^* - H_i}{\alpha_1 (t_1 - t_i)}, \quad (2)$$

where  $G$  is the mass gas flow rate, kg/s;  $S$  is the area of the phase interface,  $m^2$ ;  $k_H$  is enthalpy exchange coefficient,  $kg/m^2s$ ;  $H_g$  is air enthalpy,  $kJ/kg$ ;  $H^*$ ;  $H_i$  is the enthalpy of gas which is in equilibrium with the bulk of the solution and with the liquid on the phase interface, respectively,  $kJ/kg$ ;  $\alpha_1$  is the heat exchange coefficient from the liquid bulk to the phase interface;  $t_i$ ,  $t_1$  are the temperatures of the gas-liquid interface and the liquid bulk, respectively  $^{\circ}C$ ;  $k_g$  is mass exchange coefficient in gas,  $kg/m^2s$ .

This approach can significantly simplify the calculation of the apparatus for the heat utilization process; however, the lack of experimental data, which would allow calculating the enthalpy exchange coefficient for various trays, hinders its practical application.

### 3 Research Methodology

The study was carried out on a bench, which included an experimental apparatus, a set of auxiliary equipment, which made it possible in particular to heat the liquid, and a set of measuring instruments. The experimental apparatus consisted of a base with mounted pipelines for supplying air and draining the solution, three transparent shells having a diameter and height of 0.5 m, mounted on it, and a lid equipped with a pipeline for draining air and a device for distributing the liquid pouring into the apparatus. The researched trays were mounted between the shells. Three types of them were examined: dual-flow trays perforated with holes of 60 mm in diameter, the so-called paset or a tray in the form of a funnel with a cone mounted above it, and a baffle tray, similar in design to those used in mixing condensers. All of them were designed so that the area of the narrowest places for the passage of gas was at least 40% of the apparatus cross-section area.

We studied the dependence of the enthalpy exchanging coefficient ( $k_H$ ) to the gas velocity ( $w$ ), irrigation density ( $l$ ), liquid temperature ( $t$ ), and the design of the tray. The temperature of the initial liquid varied in the range from 60 to 90 °C, the irrigation density was from 0.2 to 5 dm<sup>3</sup>/m<sup>2</sup>s, and the gas velocity was from 0.2 to 3.5 m/s in most of the experiments. The experiments were carried out with a 15% solution of sodium chloride. On the one hand, this solution is close in properties to many real technological solutions, and, on the other hand, it is relatively accurate and simple to calculate the amount of evaporated mass by changing of the chloride ion concentration in solution.

During the initial processing of the experimental results, the enthalpy exchange coefficient was determined ( $k_H$ , see Eq. (1)). For this purpose, a particular computer program was developed to calculate the process in the experimental apparatus, which made it possible to select a value of  $k_H$ , at which the values of the calculated parameters of the liquid and gas coincided with those obtained as the result of the experiment.

### 4 Results

The estimation of the enthalpy transfer coefficient dependence on the solution temperature was initially based on the analysis of Eq. (2), which allowed us to expect that the influence of this factor will be significant. The experimental results showed that with a change in the temperature of the initial liquid in a rather wide range (of the order of 40 °C) the value of  $k_H$  decreased noticeably with increasing temperature. Still, this change turned out to be negligibly small in comparison with the impact of other factors studied. The reason for this is that, by the accepted method for calculating  $k_H$ , it was

related to the average temperature in the apparatus, and this value varied in a relatively narrow range, which depended mainly on the irrigation density. So, at  $l = 0.2 \text{ dm}^3/\text{m}^2\text{s}$ , the average temperature varied in the range of 7–9 °C, and at  $l = 5 \text{ dm}^3/\text{m}^2\text{s}$  – 15–20 °C.

When studying the impact of gas velocity and irrigation density on the enthalpy exchange coefficient, all three trays mentioned above, were included. In the range of gas velocities of 0.2–1.7 m/s in the absence of liquid accumulation on the plates, as expected, the dependencies of the enthalpy exchange coefficients on the gas velocity turned out to be qualitatively identical for all trays. In this range, slightly higher  $k_H$  values were observed at the dual-flow tray. This can be explained by the larger perimeter of holes for gas passing in comparison with the paset and the baffle tray.

With an increase in the gas velocity in the range of 2–2.5 m/s, the accumulation of liquid is on, caused by the entrainment of liquids from the lower trays to the upper ones and the formation of layers from sprays and jets. With increasing air velocity, the slope of the graphs of changes in  $k_H$  noticeably increases. This can be easily explained by the intensification of drop crushing in the constrictions of the trays (in the neck of the funnel and along the edge of the cone for the paset and in the space between the baffle tray and the wall of the apparatus) and their subsequent separation, i.e., the intensification of the renewal of the phase interaction surface. An increase in air velocity above 2.5 m/s slows down the growth of the enthalpy exchange coefficient.

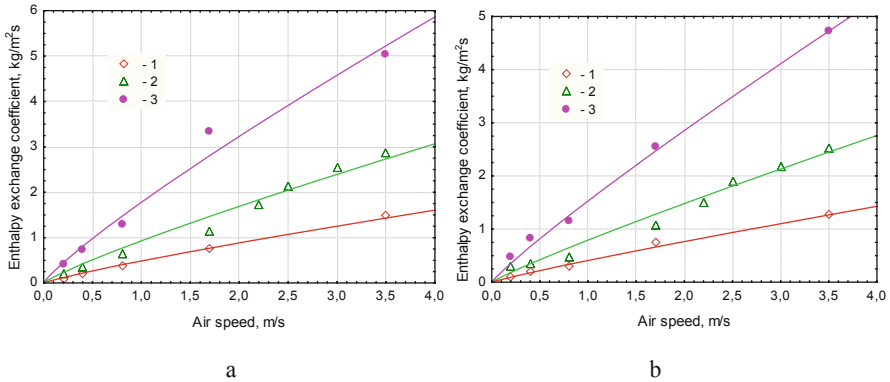
Regarding the dual-flow tray, due to the poor representation of the experimental results typical for these trays, no changes were identified in the rising of the enthalpy exchange coefficient in the range of air velocity of 2–2.5 m/s. Therefore, at higher gas velocity, the  $k_H$  value begins to “lag” the paset and baffle tray. Moreover, this “lag” reaches up to 20%. The reason for this can be judged by a slowdown in the growth of  $k_H$  with increasing air velocity from 3 to 3.5 m/s. This behaviour of the considered dependence can be explained by the longitudinal mixing of the liquid, caused by the increase of the spraying from plate to plate at these airspeeds. In contrast to the dual-flow tray, the paset and baffle tray have spray separation zones. Therefore, such spraying is much less on them.

It should be outlined that, although in contrast to the dual-flow tray, the dependencies of  $k_H$  to the gas velocity show the obvious impact of hydrodynamic regimes change for both the paset and the baffle tray, this impact is not so significant and can be neglected in the mathematical processing of the dependence of  $k_H$  to  $w$ .

Since the heat and mass exchange characteristics of the dual-flow tray are sufficiently studied and presented in the literature [3–6], further research results are presented only for the paset and baffle tray.

Figure 1a shows the dependency graph of the enthalpy exchange coefficient to the gas velocity for a paset, and Fig. 1b – for a baffle tray.





**Fig. 1.** The dependency graph of the enthalpy exchange coefficient to the air velocity for (a) paset and (b) a baffle tray at irrigation densities ( $\text{dm}^3/\text{m}^2\text{s}$ ): 1–0.2; 2–1; 3–5.

The graph lines for the paset are drawn in Fig. 1 according to the equation

$$k_H = 0,931w^{0,86}l^{0,402} \quad (3)$$

and for a baffle tray according to the equation

$$k_H = 0,793w^{0,90}l^{0,41}. \quad (4)$$

In Fig. 1, the graphs show satisfactory coincidence of the experimental points with the calculation by mentioned equations; however, without representing the hydrodynamic regimes change in the range of 1.7–2.5 m/s. Nevertheless, even with this simplification, the correlation coefficient between experiment and calculation exceeds 0.98, which can be considered as a rather reliable result.

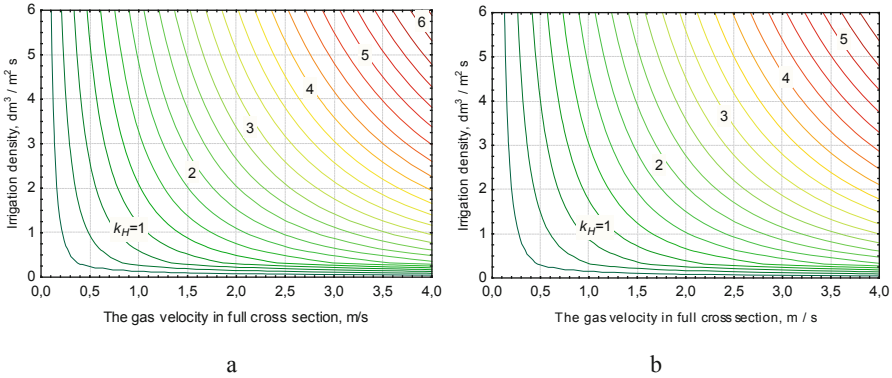
Analyzing Eqs. (3) and (4), it can be observed that the experimental data might be represented by an equation as follows:

$$k_H = b_0 \prod_{i=1}^n X_i^{b_i}, \quad (5)$$

where  $X_i$  is the factor influencing the kinetics of heat exchange (here, this is the air velocity in the entire apparatus cross-section and the irrigation density);  $b_i$  is the coefficient.

Also, the exponents at the air velocity in the entire apparatus cross-section and the irrigation density are very close for both: the paset and the baffle tray, which could be expected, concerning the resemblance of operation principles of these trays. However, the main difference between Eqs. (3) and (4) is the proportionality coefficient, which is 0.931 and 17% higher in Eq. (3) than in Eq. (4), i.e. the enthalpy exchange coefficient is significantly higher for a paset than for a baffle tray.

For further analysis, the level lines projection of three-dimensional graphs of Eqs. (3) and (4) are shown on a plane with coordinates of the gas velocity – irrigation density in Fig. 2. This figure can also be used to estimate the values of  $k_H$  for given  $w$  and  $l$ .



**Fig. 2.** The dependency graph of the enthalpy exchange coefficient on the paset (a) and on the baffle tray (b) to the air velocity in the entire apparatus cross-section and the irrigation density.

As it is shown in Fig. 2, at low air velocity, up to 0.5 m/s, the irrigation density has a somewhat slight impact on the enthalpy exchange intensity (in Fig. 2, the lines of the graphs are almost vertical in a practically applicable range of  $l$ ). However, with increasing gas velocity, the impact of irrigation density increases and at the velocity of 3.0–3.5 m/s the impact of  $w$  and  $l$  on  $k_H$  becomes approximately the same.

Comparing the obtained results with the data on the dependence of the enthalpy exchange coefficient to  $w$  and  $l$  for the dual-flow tray, obtained in work [3] in the form of the equation

$$k_H = 0,678w^{0,89}l^{0,69}, \tag{6}$$

it can be observed that the impact of the gas velocity on  $k_H$  is the same as in Eqs. (3) and (4) ( $w$  exponent is 0.89 for the dual-flow tray, and 0.86 and 0.90 are for the paset and baffle tray, respectively). Nevertheless, the impact of irrigation density on  $k_H$  is significantly higher in the dual-flow tray than in our experiments (the exponents for  $l$  are 0.69 in Eq. (5), and 0.40 and 0.41 in (3) and (4), respectively). This can be explained by separation zones in the paset and the baffle tray apparatus. Such zones appear due to the angular motion of gas and facilitate the internal circulation of the liquid, providing large liquid retardation on each tray. In contrast to the dual-flow tray, this accumulated liquid is stable on the trays. As it is shown in work [2], sprays and jets layers can arise and disappear spontaneously on a dual-flow tray under the same conditions. The mentioned above circumstances neutralize the impact of irrigation density on  $k_H$  on the dual-flow tray in comparison with the paset and baffle tray.

The analysis of Eqs. (3)–(5) shows that, in general, the enthalpy exchange coefficient is lower for the dual-flow tray than for the others, which is indicated by the lower proportionality coefficient in Eq. (5). However, due to the more significant impact of irrigation density, this difference decreases with increasing irrigation density. The calculation shows that even at  $l = 3 \text{ dm}^3/\text{m}^2\text{s}$ ,  $k_H$  for the dual-flow tray turns out to be equal to this indicator for the baffle tray, and at high irrigation density, it exceeds that, but, in the range studied, it remains less than that for the paset.

Considering the results obtained, we can conclude that paset has the best indicators of heat exchange intensity. Moreover, its main drawback is the design complexity, which leads to difficulties in cleaning from contamination and increases metal consumption in comparison with other tray researched. The dual-flow tray does not have these drawbacks. Besides, when operating at a gas velocity of less than 2 m/s, it shows results only inferior to the paset and baffles tray. However, we should beware of liquid and gas bypasses typical for large-diameter apparatuses. The baffle tray is a compromise solution and can be used in heat exchangers working with liquids containing suspensions and forming deposits on trays.

## 5 Conclusions

The paper presents the comparative study results of the thermal characteristics of trays applicable for concentrating technological and wastewater in direct contact with hot gas emissions. The dual-flow tray with large perforation, a baffle tray, similar in design to the mixing condensers, and a paset, i.e. a tray consisting of a funnel and a cone with a smaller outer diameter, set above it, were tested.

The enthalpy exchange coefficient was selected as a parameter for comparison, taking into account both “dry” (due to the temperature difference) and “wet” (due to evaporation) types of heat exchange. The degree of exposure of liquid temperature and hydrodynamic factors (gas velocity and irrigation density) to the kinetics of enthalpy exchange during the interaction between air and 15% sodium chloride solution was evaluated using this coefficient.

It was found out, that according to the degree of exposure to the heat exchange intensity, the factors are arranged in the following sequence: air velocity, related to the entire apparatus cross-section; irrigation density and temperature. Moreover, the impact of temperature appeared to be negligible. Processing the experimental results mathematically, formulas are obtained to calculate the enthalpy exchange coefficients for all tray structures researched. Recommendations are also provided for their use.

## References

1. Lage, P., Campos, F.B.: Advances in direct contact evaporator design. *Chem. Eng. Technol.* **27**(1), 91–96 (2004)
2. Pianko-Oprych, P.: Modelling of heat transfer in a packed bed column. *Pol. J. Chem. Technol.* **13**(4), 34–41 (2011)

3. Kolmetz, K., Ng, W.K., Faessler, P., Sloley, A., Zygula, T.: Distillation - 1: design guidelines outline solutions for reducing fouling in distillation columns. *Oil Gas J.* **102**(31), 60–64 (2004)
4. Domingues, T.L., Secchi, A.R., Mendes, T.F.: Overall efficiency evaluation of commercial distillation columns with valve and dualflow trays. *AIChE J.* **56**(9), 2323–2330 (2010)
5. Taranenکو, G.V.: Calculation of the lower operating limit of dual-flow plates with different geometrical characteristics. *ScienceRise* **3**(2), 67–73 (2015)
6. Taranenکو, G.V.: Hydrodynamic modeling of the operating regimes of dual-flow plates installed in columns of various diameter. *ScienceRise* **6**(35), 34–38 (2017)
7. Genić, S., Jaćimović, B., Vladić, L.: Heat transfer rate of direct-contact condensation on baffle trays. *Int. J. Heat Mass Transf.* **51**(25–26), 5772–5776 (2008)
8. Tseytlin, M.A., Rayko, V.F., Gareyev, A.T.: Contact cooling of compressed gases. In: Republican interdepartmental scientific and technical collection “Power engineering”, vol. 55, pp. 85–87. KhGPU, Khar'kov (1996). (in Russian)
9. Tseytlyn, M., Dassuky, M.: Study of the hydrodynamic characteristics of a cascade contact device. *Integr. Technol. Energy Sav.* **1**, 41–47 (2009). (in Russian)
10. Lemenand, T., Durandal, C., Della Valle, D., Peerhossaini, H.: Turbulent direct contact heat transfer between two immiscible fluids. *Int. J. Therm. Sci.* **49**(10), 1886–1898 (2010)
11. Huang, F., Zheng, J., Baleynaud, J.M., Lu, J.: Heat recovery potentials and technologies in industrial zones. *J. Energy Inst.* **90**(16), 951–961 (2017)
12. Ribeiro Jr., C.P., Lage, P.L.C.: Population balance modeling of bubble size distributions in a direct-contact evaporator using a sparger model. *Chem. Eng. Sci.* **59**(12), 2363–2377 (2004)
13. Chamat, H., Billet, A.M., Delmas, H.: Hydrodynamics and mass transfer in bubble column: influence of liquid phase surface tension. *Chem. Eng. Sci.* **62**(24), 7378–7390 (2007)
14. Narayan, G.P., Mostafa, H.S., Steven, L., et al.: Bubble columns for condensation at high concentrations of noncondensable gas: heat-transfer model and experiments. *AIChE J.* **59**(5), 1780–1790 (2013)
15. Boulama, K., Galanis, N., Orfi, J.: Heat and mass transfer between gas and liquid streams in direct contact. *Int. J. Heat Mass Transf.* **47**, 3669–3681 (2004)
16. Zezhi, Z., Abolfazl, S., Sungtaek, Y.: Thermohydraulic characteristics of a multi-string direct-contact heat exchanger. *Int. J. Heat Mass Transf.* **126**(11), 536–544 (2018)
17. Qianjian, G., Xiaoni, Q., Peng, S., Pengjiang, G.: New explicit analytical solutions of equations for heat and mass transfer in a cooling tower energy system. *Adv. Mech. Eng.* **11**(12), 1–8 (2019)
18. Estefane, P., Rayko, V.F., Tseytlyn, M.A.: The study of heat and mass transfer during the water-evaporation concentration of brine. *East.-Eur. J. Enterp. Technol.* **29**(5/1), 40–44 (2007). (in Russian)