

Biodiesel production technology using low-potential energy

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Abstract. Fatty acid esters obtained as a result of transesterification of vegetable oils or chemical reactions with alcohols are currently the main alternative fuels used in power plants. Since they do not contain aromatic hydrocarbons and sulfur compounds, emissions of CO₂, hydrocarbons, carcinogens and carcinogenic substances into the atmosphere are significantly reduced compared to fuels derived from oil. An analysis of the efficiency reserves of the most promising biodiesel production technologies shows the advantages of using supercritical fluids to isolate CO₂ from a biodiesel mixture and then separate glycerol, which is associated with environmental cleanliness, safety and energy efficiency. It is shown that the improvement of the technology of supercritical fluids for the production of biodiesel from vegetable oil can be achieved by connecting the OCF absorption-water-ammonia refrigeration unit technology to the general energy supply scheme.

1 Introduction

In accordance with the principles and criteria of "Green Chemistry", technological progress is increasingly moving towards the use of supercritical fluid technology (OCF) in various industries, since it is the safest both in production and in use due to its environmental purity. The GFR technology can be applied in the biodiesel production process to solve such tasks as waste disposal, environmental protection and reduction of material and energy costs per unit mass of the resulting product.

2 Relevance

Currently, the most common is the catalytic method of biodiesel production, the traditional method of which is considered to be catalytic transesterification reactions at atmospheric pressure, temperature 333-343 K and a molar alcohol-oil ratio of 6:1 [1, 2, 3]. However, these

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methods have disadvantages, such as the difficulty of removing the catalyst from the final product after the reaction, a long reaction time which.

3 The process of producing biodiesel fuel

In this regard, the most promising technology developed by the authors is the production of OCF biodiesel, which provides for the transesterization of vegetable oil using supercritical alcohol in a ratio of 1:10 – 1:15 at 260 °C, at a pressure of 15 MPa, collection and condensation at a temperature of 70 °C of vapors of unreacted alcohol from the reactor into an alcohol tank, extraction of the resulting reaction mixture of CO₂ under supercritical conditions at a temperature of 250 °C, a pressure of 15 MPa, cooling of the resulting biodiesel mixture to a temperature of 20 °C and separation from it first glycerin, then CO₂ vapors, followed by their condensation at a pressure of 15 MPa and a temperature of minus 40 °C and return of liquefied CO₂ to the extraction stage in the recycling, obtaining biodiesel purified from water with continuous settling of heavy and light phases in density. This technology is implemented using a steam-ejector heat pump, which provides preparation of high-temperature heat carriers [4].

The high energy consumption that occurs in the traditional industrial catalytic process for the production of biodiesel is compensated by the lack of need for the use of catalysts, the speed of the reaction and the lack of multi-stage purification of reaction products.

However, in order to reuse CO₂ in a closed thermodynamic cycle, it is necessary to carry out a process of liquefaction, which needs some detail.

Firstly, the steam-ejector heat pump operates in the region of positive temperatures and, due to limited resources, cannot provide low-temperature energy carrier preparation. And secondly, the lack of a technical solution for condensation of CO₂ in its return line followed by the production of supercritical fluids supplied to the CO₂ extraction stage hinders the industrial implementation of OCF-technologies for the production of biodiesel in the absence of a catalyst.

The aim of the work – is to increase the energy efficiency and environmental safety of the technology for producing biodiesel from vegetable oil with maximum recovery and utilization of secondary energy resources in closed thermodynamic cycles through material and heat flows using an absorption water–ammonia refrigerating machine (EARM). The connection of EARM to the general power supply scheme of OCF technology will allow low-potential energy to be generated, and CO₂ condensation to be carried out in the steady state mode of biodiesel production, and liquefied CO₂ to be directed to the extraction of the biodiesel mixture after the reesterification reaction in a closed cycle.

OCF-technology for producing biodiesel fuel from vegetable oil using EARM (Fig. 1) [5] contains reservoirs for raw materials 1 and alcohol 2, high-pressure pumps 3, 4, 28, 38; dampers 5, 39, 40, 41, 42, 43; A coil is located on the inner surface of the continuous-action transesterification reactor 6 7, with a paddle agitator 8 and a pump for pumping 9; collector 10 for products of the transesterification reaction; supercritical fluid CO₂ extractor 11 with a nozzle 12 and a switchgear 13; regenerative heat exchangers 14, 15, 16, 17; vacuum pump 18; disc separator 19; vertical gas-liquid separator 20 with inclined shelves 21, a drop trap 22 and a safety valve 23; a continuous sump for separating water from biodiesel 24; a two-stage compressor 25; a tank for liquefied CO₂ 27 installed in the CO₂ return line; a steam ejector heat pump including a steam generator 29 with electric heating elements 30 and a safety valve 31, an ejector 32, an evaporator 33, a cold receiver 34 with a refrigerant recirculation pump 35; a temperature control valve 36; a condensate collector 37; an EARM including a boiler 44, a rectifier 45, a deflegmator 46, condenser 47, evaporator 26, absorber 48 with coil, heat exchanger 49, pumping pump 50, temperature control valves 51, 52, regenerative heat exchangers 53, 54; pumps 55, 56; supply and discharge lines of material and heat flows: 1.1

At work [6, 7] the authors formulated and solved the problem of optimizing the process of transesterification of rapeseed oil with supercritical ethyl alcohol. Specific raw material and thermal energy losses in the form of:

$$R_{min} = \Pi_c \left[\frac{G_c - G_c^H - \left(\frac{P_M \left[\frac{Rt_p}{V-b} \frac{a}{(t_p+273)^{0.5} V(V+b)} \right]^{-1}}{1 - \left(\frac{P_M \left[\frac{Rt_p}{V-b} \frac{a}{(t_p+273)^{0.5} V(V+b)} \right]^{-1}} \right)} \right) \frac{M_G G_M}{M_M} \right]}{G_6} + \left[\frac{c_1 q_1 + c_2 q_2 + c_2 (N_1 + N_2 + N_3 + N_4 + N_5 + N_6)}{G_6} \right] \quad (1)$$

where C_M, C_c- are the wholesale prices of vegetable oil and alcohol, respectively, p/kg; G_M, G_c, G_c^H, G_b- respectively the mass consumption of vegetable oil, supercritical alcohol, unreacted alcohol at the outlet of the reactor, biodiesel mixture, kg/h; M_M, M_c, M_b- molar masses of vegetable oil, alcohol, biodiesel mixture, kg/mol; $\sum N$ -total thermal energy costs per unit time, r/h .

$$\sum N = c_1 q_1 + c_2 q_2 + c_2 (N_1 + N_2 + N_3 + N_4 + N_5 + N_6), \quad (2)$$

where c_1, c_2- is the cost of refrigerant, p/kg and electricity, p/ kWh; q_1- is the consumption of refrigerant for condensation of vapors of unreacted alcohol, m³/h; q_2- is the consumption of steam generator electricity to create supercritical conditions in the reactor, p/kWh; $N_1, N_2, N_3, N_4, N_5, N_6-$ respectively, the power consumption of high-pressure pumps rapeseed oil and ethyl alcohol, a stirrer drive, a biodiesel mixture discharge pump, a vacuum pump for removing excess alcohol vapors and a steam generator, kW.

Criterion (1) made it possible to continuously search for a rational loading of the transesterification reactor, ensuring a high concentration of ethyl esters of fatty acids with minimal specific raw material and energy losses under conditions of random disturbances from the quality of the starting oil and the environment.

Due to the pressure drop, the resulting biodiesel homogeneous mixture from the collection of products of the transesterification reaction 10 is fed into a supercritical fluid CO₂ extractor 11 with a nozzle 12 and a switchgear 13.

The nozzle 12 increases the contact surface of the phases, and, consequently, the mass transfer rate when mixing phases in a liquid-liquid system. Liquefied CO₂ is dispersed by means of a switchgear 13 in a stream of a continuous homogeneous mixture moving under the action of gravitational forces.

Extraction with the help of CO₂ under supercritical conditions ensures the extraction of a full range of biologically active compounds from plant raw materials.

The resulting biodiesel emulsion must be cooled to a temperature of 20 °C. For this, it is discharged from the extractor 11 into a regenerative heat exchanger 15, after which glycerin is separated from the biodiesel mixture due to centrifugal forces in the disc separator 19. After removal of glycerin, the biodiesel mixture with CO₂ vapors is fed into a vertical gas-liquid separator 20 with inclined shelves 21, a drop trap 22 and a safety valve 23; in this case, the separation of CO₂ vapors from the biodiesel mixture is carried out by gas-liquid separation due to free evaporation.

Extraction using CO₂ under supercritical conditions ensures the extraction of the full spectrum of biologically active actions from plant materials [8].

In the separator 20, by simple evaporation, CO₂ rises up, is discharged through a two-stage compressor 25 and an evaporator 26 into a tank for liquefied CO₂ 27, and biodiesel flows down inclined planes into the lower part from where it enters the sump 24 for water

separation. The droplet collector 22 is used to separate biodiesel droplets that flow down the separator through a drainage pipe. When the excess pressure in the gas-liquid separator deviates from the set value, the safety valve 23 is triggered. CO₂ vapors are removed from the gas-liquid separator 20 and subjected to compression in a two-stage compressor 25 to a pressure of 15 MPa and condensed in the evaporator of the absorption refrigeration unit 26.

The preparation of a low-potential coolant supplied to the evaporator 26 for condensation of CO₂ vapor is carried out in the EARM at a temperature of minus 40 °C. In this case, part of the high-potential steam from the steam generator 29 is sent to the boiler 44, in which the ammonia solution boils at a temperature of 130 °C. The mixture of formed water and ammonia vapors passes through the nozzles of the rectifier 45, which is irrigated with a strong aqueous ammonia solution supplied to the boiler 44 by a recirculation pump 50. Some of the water is carried away by the solution flowing down the nozzle. At the same time, the concentration of ammonia vapor increases [9].

Concentrated ammonia vapors are discharged into the deflegmator 46, the remaining water condenses and flows down the nozzles of the rectifier 45 into the boiler 44.

The drained ammonia vapor from the deflegmator 46 is sent to the condenser 47 and condensed at a temperature of 40 °C, after which the flow of liquid ammonia is throttled in the temperature control valve 51 to a pressure of 54.5 kPa and a temperature of minus 45 °C, from which it boils in the evaporator 26.

Evaporated ammonia from the evaporator 26 is fed along the 4.3 stream into the absorber 48, irrigated with a weak aqueous ammonia solution coming from the boiler 44 through a heat exchanger 49 and a temperature control valve 52. The absorption of ammonia vapors by a weak aqueous ammonia solution in the absorber 48 is accompanied by the release of heat, which is taken away by cooling water flowing through the coil of the absorber 48.

The resulting strong solution in the absorber is sent by pump 50 to the boiler 44. In the heat exchanger 49, a strong aqueous ammonia solution is preheated, going to the boiler 44 along the 4.4 stream, which leads to saving heating steam and cooling the weak aqueous ammonia solution in the 4.5 stream, providing an increase in its absorption capacity.

Recirculation of cooling water in the circuit 3.1 through the absorber 48, condenser 47 and deflegmator 46 using a pump 55 allows to increase the energy efficiency of the condensation processes of water vapor in the deflegmator 46 and ammonia vapor in the condenser 47 and ensure the removal of absorption heat from the absorber 48. Cooling water is not removed from the circulation circuit 3.1, while there is no need for periodic analysis water for the presence of ammonia in it.

Liquefied CO₂ from the evaporator 26 is discharged into the reservoir 27 and a high-pressure pump 28 is fed into the heat exchanger recuperator 17, in which it is heated to a supercritical temperature and sent to a supercritical fluid CO₂ extractor 11 in a closed cycle mode.

Biodiesel with a water content after the gas-liquid separator 20 is discharged into the sump 24, in which water is removed from it by continuous settling of the density of heavy and light phases. Purified biodiesel is discharged by a pump 56, and water from the sump 24 is sent to the condensate collector 37.

A steam-ejector heat pump is used to prepare energy carriers of different temperature potential. In the steam generator 29, high-potential steam is generated by means of electric heating elements 30 and, at a pressure of 2.0-2.5 MPa, is fed into the nozzle of the steam-ejector 32, ejecting low-potential steam at the same time, creating a reduced pressure of 0.0009-0.001 MPa and a temperature of 4-7 °C in the evaporator 33. Water is used as a refrigerant, which circulates through the cold receiver 34 using a pump 35.

The calculation of the temperature of the mixture of working and ejected vapors was based on the thermodynamic analysis of the ejector, taking into account the equations of

conservation of mass, amount of motion and energy for the mixing chamber in projections on the longitudinal axis of symmetry in the direction of movement of the main stream [10]:

$$G_p + G_3 = G_c \quad (3)$$

$$K_1 G_c v_{c2} - G_p v_{p1} - G_3 v_{31} = P_{p1} F_{p1} + P_{31} F_{31} + P_\delta F_\delta - P_{c2} F_2 - P_{cp} (F_2 - F_1) - \tau_{cp} \int_S \cos \alpha dS \quad (4)$$

$$G_p (C_{pp} T_{p1} + v_{p1}^2/2) + G_3 (C_{p3} T_{31} + v_{31}^2/2) = G_c (C_{pc} T_{c2} + K_2^2 v_{c2}^2/2) \quad (5)$$

where G_p , G_{pp} , T_{p1} , v_{p1} , P_{p1} – is the flow rate, specific heat, temperature, velocity, pressure of the working steam at the entrance to the mixing chamber; G_3 , G_{p3} , T_{31} , v_{31} , P_{31} – is the flow rate, specific heat, temperature, velocity, pressure of the ejected steam at the entrance to the mixing chamber; G_c , G_{pc} , T_{c2} , v_{c2} , P_{c2} – flow rate, specific heat, temperature, velocity, pressure of the vapor mixture at the outlet of the mixing chamber; P_δ – pressure at the ends of the ejector nozzle; F_δ – surface area of the ends of the ejector nozzle; P_{cp} – average pressure on the walls of the mixing chamber; F_1 and F_2 – cross section of the ejector at at the entrance and exit to the mixing chamber, respectively; τ_{cp} – is the average tangential stress on the walls of the mixing chamber; α – is the angle of inclination of the side surface of the mixing chamber to the longitudinal axis of symmetry in the direction of movement of the main flow; S – is the area of the side surface of the mixing chamber; K_1 , K_2 – are experimentally determined coefficients characterizing the unevenness of the density and pulsations of the flow along the cross section of the profile of the mixing chamber.

From the joint solution of equations (3-5), the parameters of the steam-air mixture at the outlet of the SEHP ejector and the geometric dimensions of the diffuser, mixing chamber and ejector nozzle were determined.

The kinetic energy of a mixture of high-potential and low-potential vapors in the ejector diffuser is converted into the thermal energy of the working steam coming out of the ejector with a pressure of 15 MPa and a temperature of 280 °C. The working steam stream 2.4 is divided into two parts, one of which is fed into the coil of the reactor 6 to create supercritical conditions for the transesterification reaction, and the other into a regenerative heat exchanger 17 to heat liquefied CO₂ to a supercritical temperature.

The spent working steam after the reactor 6 and the regenerative heat exchanger 17 is fed into the regenerative heat exchanger 16, cooled to the condensation temperature, and part of the formed condensate is discharged through a temperature control valve 36 to replenish the water level in the evaporator 33, and the other part of the condensate is sent to the condensate collector 37.

Continuously from the condensate collector 37 using a high-pressure pump 38 water is diverted to replenish the water level in the steam generator 29 with the formation of a closed cycle.

When the steam pressure in the steam generator 29 increases above the permissible level, a safety valve 31 is triggered, which relieves pressure along the flow 1.13.

The preparation of cold water with a temperature of 6-9 °C is carried out in the cold receiver 34 of a steam-ejector heat pump due to regenerative heat exchange with water recirculating through the cold receiver by means of a pump 35, and is sent to regenerative heat exchangers 14, 15, 16 for condensation of alcohol vapor, cooling of biodiesel suspension in front of a disc separator 19 and condensation of spent steam. The waste water flows after the regenerative heat exchangers 14, 15, 16 are combined and returned to the cold receiver 34 in a closed cycle mode.

Below, Tables 1,2 (appendix) provide examples of the implementation of the proposed OCF technology for the production of biodiesel for continuously operating industrial reactors with a volume of 1 m³, equipped with AVCM, for two types of oils (rapeseed and soy) and alcohols (ethyl and methyl) [11], provided that the pressure in the transesterification reactor

is 15 MPa; the pressure of CO₂ condensation after the gas-liquid separator is 15 MPa and the temperature is minus 40 °C; the temperature of liquefied CO₂ in the supercritical state is 270 °C (conditions of supercritical fluid CO₂ extraction with CO₂ recirculation in a closed thermodynamic cycle)

EARM provides energy sources for the implementation of rational temperature regimes at all stages of biodiesel production with its yield in the range of 95-97%, and creates real conditions for minimizing harmful environmental impacts on the environment.

4 Conclusion

Thus, the OCF technology for the production of biodiesel from vegetable oil under supercritical conditions using EARM makes it possible to radically reduce the operating costs of cooling and condensation of CO₂ vapors. The use of absorption refrigeration units guarantees the full use of fuel and energy resources and increases the environmental safety of the biodiesel production method. This is due to the addition of a closed recirculation circuit to the material and energy flow, which completely eliminates the discharge of spent energy into the environment.

References

1. A.A. Shevtsov, T.N. Tertychnaya, N.A. Serdyukova, V.V. Tkach, IOP Conf. Series: Earth and Environmental Science **640**, 042008 (2021). <https://doi.org/10.1088/1755-1315/640/4/042008>.
2. V.V. Hetman, N.V. Lezhneva, Herald Kazan. Technol. **8**, 124–128 (2013).
3. N.K. Kondrasheva, A.M. Yeremeyeva, Notes of the Mining Institute **260**, 248–256 (2023). <https://doi.org/10.31897/PMI.2022.15>.
4. A.A. Shevtsov, N.A. Serdyukova, K.V. Oreshin, D.S. Barabanov, V.V. Tkac No. 2,772,417 (19 May 2022).
5. A.A. Shevtsov, N.A. Serdyukova, A.M. Safin, I.V. Ledeneva, K.V. Oreshin No. 2,767,690 (18 Martha 2022).
6. V. Chirkova [et al.], Biotechnology **39**, **2**, 17–22 (2023). <https://doi.org/10.56304/S0234275823020023>.
7. R. Radermacher, Y. Hwang, Vapor compression heat pumps with refrigerant mixtures (Taylor and Francis, 2005). <https://doi.org/10.1201/9781420037579>.
8. J. Deng [et al.], Energy and Buildings **182**, 172–186 (2019). <https://doi.org/10.21122/1029-7448-2019-62-3-293-302>.
9. S.V. Alekseenko, Research and development of SB RAS in the field of energy efficiency technologies (Science, Novosibirsk, 2009).
10. V.G. Tsegelsky, Mechanical engineering **2**, 46–71 (2012).
11. K.B. Vorontsov, Chemical reactors (Editus, 2017).