Energy-efficient and environmentally friendly technology for producing fatty acid esters

A A Shevtsov¹³, T N Tertychnaya², N A Serdyukova³, V V Tkach³

¹Voronezh State University of Engineering Technology, 19, Revolution ave., Voronezh, 394036, Russia
²Voronezh State Agrarian University named after Emperor Peter the Great, 1, Michurin Str., Voronezh, 394087, Russia
³Military Training and Research Center Air force «The Air Force Academy named after professor N.E. Zhukovsky and Y. A. Gagarin», 54a, Stary Bolsheviks Str., Voronezh, 394064, Russia

E-mail: shevalol@rambler.ru

Abstract. We implemented heat pump technology of obtaining esters of fatty acids (of tolivia biodiesel) from vegetable oils, providing for the transesterification of oil with alcohol supercritical fluid and supercritical CO₂-extraction of the cooled reaction mixture, its separation by centrifugal force to separate the glycerin from the target product, the separation of carbon dioxide gas-liquid separation with obtaining a purified biodiesel and the return of carbon dioxide to the extraction stage in closed loop thermodynamic cycle. A steam-ejector heat pump is used to prepare energy carriers of different temperature potentials. The physical and chemical parameters of the obtained biodiesel fuel corresponded to the regulatory documentation. The energy and environmental efficiency of using rapeseed ethyl ether (REE) obtained using the proposed technology and its mixtures with mineral diesel fuel when performing agricultural work with the Kirovets K-701 tractor was checked. During the test, it was found that in the same operating conditions, the tractor when working on REE and its mixtures with mineral diesel fuel at maximum power develop the same traction force. The use of biodiesel and its mixtures reduces environmental pollution and increases the purity of the exhaust compared to the operation of a tractor unit using mineral diesel fuel.

1. Introduction

Fatty acid esters are an alternative fuel for various types of power plants and are obtained in chemical reactions of transesterification of vegetable oils with the participation of lower alcohols. The reaction products are fatty acid esters, which are non-toxic biodiesel fuel for various types of installations [1-2]. Due to the absence of aromatic hydrocarbons and sulfur compounds in biodiesel, the emission of carbon dioxide, hydrocarbons, carcinogens, and soot into the atmosphere is significantly reduced compared to diesel fuel obtained from oil. Biodiesel fuel is characterized by a higher cetane number (on average, 54-58 units), a high flash point (above 100 °C), and a better lubricity [2].

Analysis of the efficiency reserves of the most promising technologies for producing biodiesel showed the feasibility of implementing the technological cycle in the following sequence: first, the transesterification of vegetable oil with supercritical alcohol is carried out, then the fluid supercritical
CO₂ extraction of the cooled reaction mixture; its separation in the field of centrifugal forces for separating glycerol, and then the separation of carbon dioxide by gas-liquid separation to obtain purified biodiesel and return carbon dioxide to the extraction stage [3-4].

Supercritical fluid extraction is based on the unique properties of the solvent (carbon dioxide) to extract soluble components under certain (supercritical) thermodynamic parameters. The main characteristic of supercritical fluids is the absence of a liquid-vapor (gas) phase transition and the possibility of continuous changes in the density, viscosity, and other properties of the homogeneous fluid over a wide range when the pressure changes, which allows you to influence the properties of carbon dioxide as a solvent. While in a supercritical state, the fluid (from ang. «fluid», that is, «capable of flowing») is something intermediate between a liquid and a gas. It can be compressed as a gas (ordinary liquids are almost incompressible) and, at the same time, is able to dissolve substances, which is not typical of gases [5-7].

In the technology of complex processing of vegetable oil, heat pumps are increasingly used, which allow one to bring the operation of equipment to high energy perfection in relation to the use of energy carriers [8-11].

Despite the obvious advantage of known technologies associated with the transesterification process in supercritical conditions, which provide a significant reduction in the reaction time of transesterification in the absence of catalyst decomposition products and a high conversion of vegetable oil to biofuel (>95 %), they do not allow for joint processes of transesterification of vegetable oil with alcohol and separation of biodiesel from glycerol by CO₂ extraction in supercritical conditions using a heat pump, and therefore, they do not solve the most important tasks of reducing the specific energy consumption for the production of biodiesel, improving its quality and environmental cleanliness of the entire production cycle.

The purpose of this work is to improve the energy efficiency and environmental safety of the method 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 a steam-ejector heat pump.

2. Method for improving energy efficiency

In order to achieve this objective, an energy-efficient and environmentally friendly technology for producing biodiesel fatty acid esters is proposed, the scheme of which is shown in Fig. 1 [12].

The scheme contains pressure tanks for vegetable oil 1 and alcohol 2, high-pressure pumps 3, 4, 28, 38; flaps 5, 39, 40, 41, 42, 43; continuous transesterification reactor 6 with a coil 7 located on the inner surface, with a paddle agitator 8 and a pumping pump 9; a collection of products of the transesterification reaction 10; a supercritical fluid CO₂ extractor 11 with a nozzle 12 and a distribution device 13; recuperative heat exchangers 14, 15, 16, 17; a vacuum pump 18; a disc separator 19; vertical gas-liquid separator 20 with inclined shelves 21, a drop catcher 22 and a safety valve 23; a continuous sump for separating water from biodiesel 24; a two-stage compressor 25; an evaporator of the refrigeration unit 26 and a tank for liquefied carbon dioxide 27 installed in the carbon dioxide return line; a steam-ejector heat pump including a steam generator 29 with electric heating elements 30 and a safety valve 31, a steam-steam ejector 32, an evaporator 33, cold collector 34 with refrigerant recirculation pump 35; thermal control valve 36; condensate collector 37; lines for supplying and removing material and heat flows: 1.1 – vegetable oil; 1.2 – alcohol; 1.3 – a mixture of products of the transesterification reaction; 1.4 – vapors of excess alcohol; 1.5 – excess alcohol; 1.6 – biodiesel homogeneous mixture; 1.7 – biodiesel emulsion; 1.8 – biodiesel mixture with carbon dioxide vapors; 1.9 – glycerol; 1.10 – biodiesel fuel with water content; 1.11 – purified biodiesel fuel; 1.12 – water; 1.13-carbon dioxide vapors, 1.14-liquefied carbon dioxide 1.15-heated liquefied carbon dioxide; 2.1-high-potential steam; 2.2-ejected low-potential steam; 2.3-water recirculation through the cold receiver; 2.4-working steam; 2.5-waste steam; 2.6-condensate; 3.1 – cold water; 3.2 – waste water; 4.1 – liquid refrigerant; 4.2 – refrigerant vapor.

The technological cycle of biodiesel production is implemented as follows.
From the pressure tanks 1 and 2, high-pressure pumps 3 and 4 in a given ratio of 1:10-1:15 feed vegetable oil and alcohol to the continuous re-etherification reactor 6 with a coil 7 located on the inner surface and a paddle stirrer 8.

**Figure 1.** Process diagram of biodiesel production
In reactor 6, the necessary conditions are created for the reaction of transesterification of vegetable oil with alcohol at a temperature of 250-280 °C and a pressure of 15-17 MPa. In this case, the mixture in the reactor is mixed to a homogeneous state and heated to a supercritical state of alcohol due to the presence of a coil into which the working steam is fed at a temperature of 260-290 °C. The mixture of products of the transesterification reaction by the pumping pump 9 is withdrawn from the reactor 6 to the collector 10. The excess alcohol vapors are removed to the recuperative heat exchanger 14 using the vacuum pump 18, condensed, and the excess alcohol is returned to the reservoir 2. Due to the pressure drop, the resulting biodiesel homogeneous mixture from the collection of products of the transesterification reaction 10 is fed to a supercritical fluid CO$_2$ extractor 11 with a nozzle 12 and a distribution device 13.

The resulting biodiesel emulsion from the extractor 11 is diverted to a recuperative heat exchanger 15, in which it is cooled to a temperature of 20-30 °C and fed to a disc separator 19 to separate the glycerol from the biodiesel mixture in the field of centrifugal forces. The glycerine is withdrawn, and the biodiesel mixture with carbon dioxide vapor is fed to a vertical gas-liquid separator 20 with inclined shelves 21, a drop catcher 22, and a safety valve 23. In this case, the separation of carbon dioxide vapors from the biodiesel mixture is carried out with free evaporation by gas-liquid separation. Biodiesel flows down the inclined shelves 21 to the lower part of the separator 20. Carbon dioxide rises and is removed from biodiesel by simple evaporation. The drop catcher 22 is used to separate the biodiesel drops that flow down the separator through the drainage pipe. If the excess pressure in the gas-liquid separator deviates from the set value, the safety valve 23 is activated.

Carbon dioxide 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 at a temperature of minus 40 °C in the evaporator 26 of the refrigeration unit.

The liquefied carbon dioxide is discharged to the reservoir 27 and fed by a high-pressure pump 28 to the heat exchanger recuperator 17, in which it is heated to a supercritical temperature and sent to the supercritical fluid CO$_2$ extractor 11 in a closed cycle mode.

Biodiesel with a water content after the gas-liquid separator 20 is diverted to the sump 24, where water is removed from it by continuous sedimentation of the heavy and light phases. In this way, purified biodiesel is obtained, 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. 29 in the steam generator with electric heating elements 30 is produced of high-potential and vapor pressure 2.0 – 2.5 MPa is supplied to the nozzle is a steam-steam ejector 32, ejective in this low-grade steam from the evaporator 33, creating it a negative pressure of 0.0009–0.001 MPa and temperature of 4 - 7 °C. The refrigerant is water circulating through halodapini 34 with a pump 35.

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 vapor exiting the ejector with a pressure of 15 MPa and a temperature of 280 °C. The working vapor Stream 2.4 is divided into two parts, one of which is fed to the reactor coil 6 to create supercritical conditions for the transesterification reaction, and the other to the recuperative heat exchanger 17 to heat the liquefied carbon dioxide to supercritical temperature.

The spent working steam after the reactor 6 and the recuperative heat exchanger 17 is fed to the recuperative heat exchanger 16, cooled to the condensation temperature, and part of the formed condensate is withdrawn through the 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.

Water is continuously withdrawn from the condensate collector 37 using a high-pressure pump 38 to replenish the water level in the steam generator 29 to form a closed cycle.

If the steam pressure in the steam generator 29 increases above the permissible level, the safety valve 31 is activated.

Preparation of cold water with a temperature of 6 - 9 °C is carried out in headpiece 34 steam jet heat pump through recuperative heat exchange with water and sent to the regenerative heat exchangers.
14, 15, 16, respectively, for the condensation of alcohol vapor, cooling the biodiesel suspension front disc separator 19, the condensation of exhaust steam. The wastewater flows after the recuperative heat exchangers 14, 15, 16 combined and returned to holoprint 34 in a closed loop cycle.

3. Results

The technology is implemented to produce rapeseed ethyl ether (biodiesel) from vegetable oil on an experimental line with a capacity of 300 l/h for the original rapeseed oil in the production conditions of Zolotaya Niva LLC in the Verkhnekhavsky district of the Voronezh region.

Rapeseed oil was mixed with ethyl alcohol at a volume ratio of 1:12 to a homogeneous state in the working volume of the reactor and transesterified at a temperature of 260 °C and a pressure of 15 MPa. The excess alcohol vapors were condensed at a temperature of 70 °C. The resulting reaction mixture was extracted with carbon dioxide under supercritical conditions at a carbon dioxide flow rate of 20 l/h, a temperature of 250 °C, and a pressure of 15 MPa. Extraction of the resulting reaction mixture with carbon dioxide under supercritical conditions was performed at a temperature of 250 °C and a pressure of 15 MPa. The biodiesel mixture was cooled to a temperature of 20 °C and fed to separators first to separate glycerol in the field of centrifugal forces, and then carbon dioxide by gas-liquid separation.

The extracted carbon dioxide vapors were condensed at a pressure of 15 MPa and a temperature of minus 40 °C, and then returned to the extraction stage. After separation of water by continuous sedimentation for the density of heavy and light phases, its content in biodiesel did not exceed 200 mg/kg. The yield of biodiesel was 96 wt.% when energy consumption per unit mass of the target product is 14.5 kWh/l with an average electricity price of 4.5 rubles/kWh; the cost of one liter of biodiesel was 65.25 rubles.

Energy-efficient modes of technological processes in the field of acceptable properties of the target products were carried out using a steam-ejector heat pump with the following parameters:

| Parameter                                           | Value |
|-----------------------------------------------------|-------|
| Cooling Capacity, W                                 | 20    |
| Boiling point                                       |       |
| - in the evaporator, °C                             | 4     |
| - in the steam generator, °C                        | 110   |
| The temperature of the working pair                 |       |
| at the entrance to the cooling coil of the reactor  | 280   |
| °C                                                  | 6     |
| Ejection coefficient                                | 92    |
| Heat transfer coefficient                           |       |
| cold receiver, W / m² · °C                         |       |
| Area of heat exchange surfaces, m²                  | 8     |
| - cold receiver, m²                                 | 6     |
| - reactor coil                                      |       |
| - regenerative heat exchanger                        | 4     |
| for heating liquefied carbon dioxide                 |       |
| Refrigerant                                         | water |

The design of the steam-ejector heat pump does not contain moving wear-out elements, which ensures trouble-free operation of the pump for long cycles without direct maintenance. At the same time, the volume of current repairs, the cost and the need for spare parts and auxiliary materials are minimized.

High-potential steam was obtained in an electric steam generator «Ural-Power», which is able to produce saturated and superheated steam up to 400 °C and a pressure of up to 140 kgf/cm².
In the recirculation loop, the steam jet heat pump used steam-steam ejector (thermocompressor) of type PKS provides a return to the system of working pair and its reuse with the required parameters. The scale of energy saving when using a thermocompressor is significant, since it allowed the system to completely return low-potential steam, usually discharged into the atmosphere, and avoid losses associated with throttling and regulating steam flows. The use of a thermocompressor reduced technological emissions to a minimum and made it possible to completely avoid environmental pollution from the discharge of waste heat carriers.

Physical and chemical parameters of the obtained biodiesel fuel correspond to the interstate standard GOST 305–2013 «Diesel Fuel. Technical conditions» and are shown in table 1.

| №  | Indicators                                    | Value   |
|----|----------------------------------------------|---------|
| 1  | Cetane number                                | 49      |
| 2  | Kinematic viscosity at 20°C, mm²/s           | 4.2     |
| 3  | Flash point, °C                              | 80      |
| 4  | Mass fraction of sulfur, mg/kg               | 1000    |
| 5  | Mass fraction of moisture, mg/kg             | 190     |
| 6  | Acidity, mg per 100 cm³ of fuel              | 2.0     |
| 7  | Density at 15 °C, kg/m³                      | 842     |

The energy and environmental efficiency of using rapeseed ethyl ether (biodiesel) was obtained using the proposed technology, and its mixtures with mineral diesel fuel in the ratio of 30:70 and 50:50 when performing agricultural work with a tractor «Kirovets» K-701 with a diesel power of 220.6 kW (300 HP).

During the inspection, it was found that the specific consumption of pure rapeseed ethyl ether is 9% higher than that of mineral diesel fuel. When working with fuel mixtures in the ratio of 50% and 30%, fuel consumption was higher by 6.0% and 4.0%, respectively. Under the same operating conditions, the tractor develops the same traction force when working on rapeseed ethyl ether and its mixtures with mineral diesel fuel at maximum power. The use of biodiesel and its mixtures reduces environmental pollution of carbon monoxide, increases the purity of the exhaust compared to the operation of a tractor unit on mineral diesel fuel.

4. Discussion

Rational use of heat and electric energy in the cold and heat supply system using a steam-ejector heat pump was considered from the point of view of reducing the cost of the resulting target and intermediate products. The main principle solution for reducing energy consumption in the proposed method is the optimal choice of the current values of the working steam and cold-water temperatures. Deviation from these values will inevitably lead to an increase in energy consumption. Lowering the boiling point of the refrigerant in the evaporator by 1°C will lead to the need to increase the flow of working steam to the ejector, and consequently, to an energy overspend of 5–7 %, and increasing the condensation temperature by 1°C will lead to an increase in energy consumption by 7.0–10.0 % [13].

The proposed technology for producing biodiesel expands the boundaries of energy-efficient coupling of objects of different temperature potentials based on the utilization and recovery of secondary energy resources. At the same time, a universal approach has been fully implemented in creating a competitive technology that provides heat and cold generation for jointly occurring processes in the production of biodiesel from vegetable oil.
5. Conclusion
The proposed technology allows one to reduce specific energy consumption by 10–12% due to the rational use of energy carriers using a steam-ejector heat pump. It creates environmentally safe conditions for implementation by using water as a working medium in steam-ejector heat pump, excluding the use of toxic, explosive and fire-hazardous working environments, as well as by organizing closed recycling schemes for material and energy flows with a significant reduction in the removal of secondary energy resources from the heat and cold supply scheme.

References
[1] Anikeev B I and Yakovleva E Yu 2012 Transesterification of rapeseed oil in supercritical methanol in flow reactor Journal of physical chemistry 86 (11) 1766–1774
[2] Markov B A, Nine Nin C H, Semenov B G, Shahov A B and Bagrov 2011 Use of commercial oils and fuels based on them in diesel engines (Moscow: LLC NIC «Ingener» (Union of NIO), LLC «Oniko-M»)
[3] Vinokrov V A, Dudashev M N and Barkalov A V 2010 RF, Patent No/ № 2412236, C11C 3/04. The ability of the obtained biodiesel (20.06.2010)
[4] Ilchibakieva E U, Filenko D G, Barkov A V, Dudashev M N and Vinokrov B A 2010 Supercritical transesterification of rapeseed oil Ecology of industrial production 4 66–69
[5] Dadashev M N, Kukharenko A A, Grigoriev B A, Alkatseva N I and Novoseltsev D V 2005 Supercritical fluid extraction - technology of the XXI century Storage and processing of agricultural raw materials 1 15–16
[6] Kasyanov G I, Stasieva O N and Latin N N 2005 Do- and supercritical extraction: benefits and shortcomings Food industry 1 36–39
[7] Ivakhnov A D, Scrubets T E, Bogdanov M V and Bogolitsyn K G 2013 Production of rapeseed oil by extraction with supercritical carbon dioxide Chemistry of plant raw materials 3 137-141
[8] Shevtsov A A, Bunin E C, Tkach V V, Serdyukova H A and Fononov D I 2018 Effective implementation of a steam compression heat pump in the line of complex processing of oilseeds Storage and processing of agricultural raw materials 1 60–64
[9] Shevtsov A A, Tertychnaya T N, Tkach V V and Serdyukova N A 2019 Energy-saving technology for extracting protein-containing fractions from oilseeds using a steam-ejector heat pump newspaper of the Voronezh state University of engineering technologies 2 35–40
[10] Shevtsov A A, Tkach V V, Saltykov S N, Serdyukova N A and Kopylov M V 2018 RF, Patent No. 2688467 C1, IPC C11B 1/06. Method for managing a line for complex processing of oilseeds (21.05.2019)
[11] Shevtsov S A, Tkach V V, Tertychnaya T N and Serdyukova N A RF, Patent No. 2693046 C1, IPC C11B 3/04, C11C 3/10, C10L 1/02, C07C 67/03. Method for managing the process of processing oilseeds into biodiesel (01.07.2019)
[12] Tertychnaya T N, Shevtsov S A, Tkach V V and Serdyukova N A 2019 RF, Patent No. 2714306 C1, IPC C11C 3/10, C10L 1/02, C10G 3/00, C07C 67/02. A method of producing biodiesel and installation for its implementation (14.02.2020)
[13] Bambushkov E M, Bukharin N and Gerasimov E D 1987 Thermal and structural calculations of refrigerating machines Under the general edition of I A Sakuna (Leningrad: Mechanical Engineering, Leningrad Branch)