**Ethyl acetate production by the method of ethanol dehydrogenation**

**by Manufacturing Group Techinservice Limited**

Method patent of ethyl acetate production No. 2650890 as of April 18, 2018 (RU)

Method patent of ethyl acetate production No. 116827 as of October 05, 2018 (UA)

Ethyl acetate is a widely used solvent putted to use in the paints’ manufacturing, drug preparation, printing inks for the food industry. The last line consumes up to 30% of the total produced ethyl acetate, which is due to its very low toxicity. World production of ethyl acetate in 2006 was about 1.2 million tons. In Russia, production of ethyl acetate in 2010 reached 30 thousand tons per year, and all of ethyl acetate was produced by ***etherification of acetic acid by dry ethanol with sulfuric acid.*** Due to the high corrosivity of acetic and sulfuric acids, most of the equipment in this process is made of heat-resistant steel. In addition, during the esterification process the water is originated, therefore, it subsists a necessity for ***wastewater disposal.***

The interacting of acetic acid with ethanol is an equilibrium process:

CH3COOH + C2H5OH ↔ CH3COOCH2CH3 + H2O

The water occurrence shifts the balance to the left, and as a result reduces the concentration of ethyl acetate. To reduce this effect, dried ethanol is used in the process, which requires additional equipment and energy consumption.

The second method of ethyl acetate production is ***the dehydrogenation of ethanol*** by the following reactions:

С2H5OH ↔ C2H4O + H2

С2H5OH + C2H4O ↔ CH3COOCH2CH3 + H2

It is also an equilibrium process. The advantage of this method is the usage of only one type of raw material ***ethanol***. At the same time, ***bioethanol*** may be entrained in the process, which includes the production of ethyl acetate in the field of "green" chemistry and bases it ***on renewable sources of raw materials***. It should be noted that in this method of producing ethyl acetate, the intermediate product is acetaldehyde. However, it is not a co-product, the formation of which leads to non-recoverable loss of the raw material, since it is converted either into ethyl acetate that is a desired reaction product, or (at the next stage) its hydrogenates into ethanol that is the raw material. Above mentioned, allows us to conclude that the process of producing ethyl acetate by dehydrogenating ethanol is of practical interest, because it:

1) excludes work with aggressive **sulfuric acid**;

2) uses ***only one substance*** as a raw material - ethanol and may be involved in the field of "green chemistry" through the use of renewable raw materials - bioethanol;

3) can be organized at relatively small enterprises.

Due to this, Techinservice carried out work on the determination of the conditions of this process and the selection of the catalyst. The catalyst developed by Techinservice provides 43% alcohol conversion with 84% selectivity for ethyl acetate. The yield of ethyl acetate is 36%. At the same time, 57% of ethanol can be returned from recycling.

Conditions of the technological process of Techinservice:

temperature in the 1st stage (reactor): 230-240 °C

pressure in the 1st stage (reactor): 4,0-6,0 barg

temperature in the 2nd stage (reactor): 160-180 °C

pressure in the 2nd stage (reactor): 12,0-15,0 barg

**1 Material Balance**

Operating hours (calculated as 100% capacity) 8,000

|  |  |  |
| --- | --- | --- |
| **Product** | **Capacity** | **Unit** |
| Ethyl Acetate (EA) | 50,000 | mt/a |
| Ethyl Acetate (EA) | 6 250 | kg/h |
|  |  |  |
| Light Fraction | 620 | mt/a |
| Light Fraction | 77.5 | kg/h |
|  |  |  |
| Heavy Fraction | 5984 | mt/a |
| Heavy Fraction | 748 | kg/h |
|  |  |  |
| Waste water | 1725 | mt/a |
| Waste water | 215.65 | kg/h |
|  |  |  |
| Hydrogen | 2837 | mt/a |
| Hydrogen | 354.6 | kg/h |
| **Total** | **61,166** | **mt/a** |
| **7646** | **kg/h** |
|  | | |
| **Total Feed**  (Ethanol 99.5 %wt) | **61,166** | **mt/a** |
| **7646** | **kg/h** |

**2 Consumptions**

**2.1 Feedstock**

***Major Feedstock’s (average values unless indicated otherwise)***

Operating hours 8,000

Dewatering Ethanol (at 100%)1) mt/a 60,860

Dewatering Ethanol (at 100%)1) t Et/t EA 1.217

Ethylene Glycol (at 100%) kg/t EA 0.03

Catalyst (2 Years Lifetime) kg/t EA 0.1452)

Hydrogenation Catalyst (2 Years Lifetime) kg/t EA 0.153)

1) As 99.5 wt% Ethanol/Water mixture;2) catalyst density of 1.2 kg/l;3) Depending on the type of catalyst

**2.2 Utilities**

***Utilities (average values unless indicated otherwise)***

Operating hours (calculated as 100% capacity) 8000

Steam (5 barg) t/t EA ≤21)

Steam (5 barg) kg/h 12 t/h1)

Natural Gas2) Nm3/t EA 52.83)

Natural Gas2) Nm3/h 3303)

Cooling Water

(max 30°C Supply, Return 42°C) m3/t EA 240

Cooling Water

(max 30°C Supply, Return 42°C) m3/h 1500

Chilled Water

(Supply minus 30°C, Return minus 25°C)4,5) m3/t EA 3.2

Chilled Water

(Supply minus 30°C, Return minus 20°C)4,5) m3/h 20

Heat Transfer Fluid t/t EA 72

Instrument Air Nm3/t EA 8

Nitrogen average Nm3/t EA 10

Electricity kWh/t EA 50

1) Using produced hydrogen and additional natural gas as fuel in Fired Heater; 2) Lower Heating value not less 34 MJ/m3; 3) at normal conditional (1.01325 bara, 0 °C); 4) Chilled Water unit is part of EA Plant investment; 5) As aqueous solution 50 wt% Ethylene glycol

**3 EA Product & Co-product Specification**

**3.1 Standard Specification of EA**

|  |  |  |  |
| --- | --- | --- | --- |
| **Property** | **Unit** | **Value** | **Method** |
| Colour | Pt-Co | ≤10 | ASTM D1209 |
| Water | % | ≤0.03 | ASTM D1364 |
| Density at 20°C | g/cm3 | 0.899-0.901 | ASTM D4052 |
| Ethanol content | % | ≤0.05 | GC |
| Purity | % | ≥99.7 | GC |
| MEK | % | ≤0.3 | GC |
| Acidity | % | ≤0.005 | ASTM D1613 |
| Distilation Range | °C | 75.5-79.5 | ASTM D1078 |

**3.2 Light Fraction Composition**

|  |  |  |
| --- | --- | --- |
| **Components** | **Unit** | **Value** |
| Diethyl Ether | %wt | 58.08 |
| Ethyl Acetate | %wt | 30.74 |
| Acetaldehyde | %wt | 1.47 |
| Ethanol | %wt | 7.04 |
| Water | %wt | 2.67 |

**3.3 Heavy Fraction Composition**

|  |  |  |
| --- | --- | --- |
| **Components** | **Unit** | **Value** |
| n-Butyl Acetate | %wt | 12.948 |
| 1-Butanol | %wt | 19.480 |
| 2-Butanol | %wt | 66.570 |
| Ethanol | %wt | 1.000 |
| Water | %wt | 0.002 |

**3.4 Hydrogen Composition**

|  |  |  |
| --- | --- | --- |
| **Property/Components** | **Unit** | **Value** |
| Diethyl Ether | %vol | 0.0560 |
| Ethyl Acetate | %vol | 0.0677 |
| Ethanol | %vol | 0.0186 |
| Acetaldehyde | %vol | 0.6500 |
| MEK | %vol | 0.0061 |
| Water | %vol | 0.0016 |
| Hydrogen | %vol | 99.2 |
| **Lower Heating value** | **MJ/m3** | **10.9** |
| **Density** | **kg/m3** | **0.0884** |

**3.5 Waste Water**

|  |  |  |
| --- | --- | --- |
| **Property/Components** | **Unit** | **Value** |
| Ethyl Acetate | %wt | 0.080 |
| Ethanol | %wt | 0.405 |
| Ethylene glycol | %wt | 0.010 |
| MEK | %wt | 0.010 |
| Water | %wt | 99.495 |

**4 Equipment Specification**

|  |  |
| --- | --- |
| **Position** | **Name** |
| 1R01/1 | Ethanol Dehydrogenation Reactor |
| 1R01/2 | Ethanol Dehydrogenation Reactor |
| 1R02/1 | Hydrogenation Reactor |
| 1R02/2 | Hydrogenation Reactor |
| 1Т01 | EA Cut Column |
| 1Т02 | EA Purification Column |
| 1Т03 | Ethanol Purification Column |
| 1Т04 | Ethanol Recovery Column |
| 1Т05 | EG Recovery Column |
| 1E01/1 | Reboiler Column 1.Т01 |
| 1E01/2 | Reboiler Column 1.Т01 |
| 1E02 | Reboiler Column 1.Т02 |
| 1E03/1 | Reboiler Column 1.Т03 |
| 1E03/2 | Reboiler Column 1.Т03 |
| 1E04 | Reboiler Column 1.Т04/ Condenser Column 1.Т02 |
| 1E05 | Reboiler Column 1.Т05/ Condenser Column 1.Т02 |
| 1E06 | Condenser Column 1.Т01 |
| 1E07 | Condenser Column 1.Т02/Ethanol evoporator |
| 1E08 | Condenser Column 1.Т03 |
| 1E09 | Condenser Column 1.Т04 |
| 1E10 | Condenser Column 1.Т05 |
| 1E11 | Ethanol Superheater |
| 1E12 | Recuperator reaction product |
| 1E13 | Recuperator reaction product |
| 1E14 | Water Cooler reaction product |
| 1E15 | Chilled Water Cooler |
| 1E16 | Chilled Water Cooler |
| 1E17 | Recuperator reaction product |
| 1E18 | Superheater reaction mixture |
| 1E19 | EA/Ethanol Recuperator |
| 1E20 | EA Recuperator |
| 1E21 | EG Recuperator |
| 1E22 | EA/Ethanol Recuperator |
| 1E23 | EA/Dewatering Ethanol Recuperator |
| 1E24 | Dewatering Ethanol/ Heavy Fraction Recuperator |
| 1E25 | Light Fraction Cooler |
| 1E26 | EA Cooler/Hydrogen Heater |
| 1E27 | Heavy Fraction Cooler/Hydrogen Heater |
| 1E28 | Heavy Fraction Cooler |
| 1E29 | Chiller |
| 1H01 | Fired Heater |
| 1P01 | Reflux Pump 1.T01 |
| 1P02 | Reflux Pump 1.T02 |
| 1P03 | Reflux Pump 1.T03 |
| 1P04 | Reflux Pump 1.T04 |
| 1P05 | Reflux Pump 1.T05 |
| 1P06 | 1T03 Column Feed Pump |
| 1P07 | EA Pump |
| 1P08 | Heavy Fraction Pump |
| 1P09 | 1T05 Column Feed Pump |
| 1P10 | EG Recycle Pump |
| 1P11 | 1T02 Column Feed Pump |
| 1P12 | Ethanol Evapotor Feed Pump |
| 1P13 | Reaction product Pump |
| 1P14 | HTO Pump |
| 1P15 | HTO Pump |
| 1P16 | Emergency Pump |
| 1P17 | Draine Pump |
| 1P18 | Cooalant Pump |
| 1P19 | Light Fraction Pump |
| 1К01 | Vacuum Pump |
| 1К02 | Hydrogen Compressor |
| 1D01 | Reflux Drum 1.T01 |
| 1D02 | Reflux Drum 1.T02 |
| 1D03 | Reflux Drum 1.T03 |
| 1D04 | Reflux Drum 1.T04 |
| 1D05 | Reflux Drum 1.T05 |
| 1D06 | Ethanol evaporation Drum |
| 1D07 | Reaction product Drum |
| 1D08 | HTO Recycle Drum |
| 1D09 | HTO Recycle Drum |
| 1D10 | EG Recycle Drum |
| 1D11 | 1T02 Column Feed Drum |
| 1D12 | Light Fraction Drum |
| 1D13 | Cooalant Recycle Drum |
| 1D14 | Emergency Drum |
| 1D15 | Draine Drum |
| 1D16 | Vacuum Pump Drum |