Mathematical model of the production of highly purified stable oils with ultra-high viscosity index

D M Sigaeva¹, I V Akhmetov¹, R M Uzyanbaev¹,2 and I M Gubaydullin¹,3

¹Ufa State Petroleum Technological University, Kosmonavtov St. 1, Ufa, Russia, 450062
²National Research Mordovia State University, Bolshevistskaya St. 68, Saransk, Russia, 430005
³Institute of Petrochemistry and Catalysis of the Russian Academy of Science, Prospekt Oktyabrya St. 141, Ufa, Russia, 450075

e-mail: dashasigaeva@mail.ru, ravil-11@mail.ru, irekmars@mail.ru

Abstract. In the last decade the world has a clear desire to force the modes of operation of internal combustion engines: improving the calorific intensity, compression in the cylinders, the crankshaft rotation speed. So, medium-purified oils are increasingly replaced at the world market by highly-purified stable oils with an ultra-high viscosity index and quality giveaway. In order to increase the competitiveness of domestic oils, in particular engine oils, two ways of improvement of technological processes have been developed. First: improved solvent cleaning processes, including the introduction of a new selective solvent N-methylpyrrolidone, to make oil with a viscosity index of 95 to 100 produced from selected crude oils; accelerated production of synthetic oils with improved properties of polyester and polysiloxane oils etc. Second: increased inclusion of hydrogenation processes with highly selective catalysts for the production of oils with a viscosity index above 100 produced from broad-grade oils. In this paper we have developed a project of a selective oil purification plant using N-methylpyrrolidone solvent. We have developed a mathematical model and use the computer simulation to calculated the material and heat balances of the process, main and auxiliary equipment.

1. Introduction

At present, the majority of the world production of oils is accounted for by the oils made of mineral base oils produced according to the traditional technology (solvent refining), this is why a plant for selective oil purification by selective solvents is an integral part of a modern fuel and lube refinery [1-3].

The selective oil purification plant is designed to remove resins and asphaltic compounds, polycyclic and naphthenic aromatic hydrocarbons with short side chains, and sulfur-containing compounds from the oil fractions by way of extraction with polar solvents in order to improve the chemical composition, viscosity-temperature and antioxidant properties, to increase the viscosity index, to reduce coking ability, carbon and lacquer-forming properties [4, 5].

Significant experience in operation of selective oil purification plants with selective solvents has shown that under equal conditions in terms of technical equipment, the improvement of technical parameters of the process is achieved by using N-methylpyrrolidone solvent [6-8].

Feedstock for the selective oil purification plant is the distillate fraction 350-420°C.

The plant crude capacity is 675 t/day. The selection of raffinate is 54% of the feed.
The ratio of N-methylpyrrolidone to the feed is 2:1 (by weight) [9-12].

Extraction column temperature:
- Extraction - 73°C;
- top - 80°C;
- bottom - 65°C.

Density:
- distillate - 915 kg/m³;
- raffinate - 870 kg/m³;
- extract - 975 kg/m³;
- N-methylpyrrolidone - 1030 kg/m³.

Molecular weight:
- N-methylpyrrolidone – 99.13.

Feed temperature:
- N-methylpyrrolidone – 80 °C;
- feedstock – 60 °C.

On the basis of these data, the material balance of the plant was developed (Table 1).

### Table 1. Material balance of the plant.

| Feedstock and products          | Quantity, t/year | % of the total |
|---------------------------------|------------------|----------------|
| Taken:                         |                  |                |
| Feedstock fraction 350-420°C    | 230000.0         | 100.00         |
| Total                          | 230000.0         | 100.00         |
| Produced:                      |                  |                |
| Raffinate                      | 124200.0         | 54.00          |
| Extract                        | 104673.0         | 45.51          |
| Losses                         | 1127.0           | 0.49           |
| Total                          | 230000.0         | 100.00         |

### 2. Extraction column model

The extraction column is designed to purify oil of unwanted components using N-methylpyrrolidone. The column operates according to the countercurrent principle [13-15]. The solvent to the feedstock ratio is 2:1. The composition of the raffinate solution was defined on the basis of practical data.

### 2.1. Material balance of the extraction column

#### Table 2. Material balance of the extraction column.

| Feedstock and products          | t/year | t/day   | kg/hour  | mass % of the feedstock |
|---------------------------------|--------|---------|----------|--------------------------|
| Taken:                         |        |         |          |                          |
| Feedstock fraction 350-420°C    | 230000.0 | 676.47  | 28186.25 | 100.00                   |
| N-methylpyrrolidone             | 460000.0  | 1352.94 | 56372.5  | 200                       |
| Total                          | 690000.0  | 2029.41 | 84558.75 | 300.00                   |
| Produced:                      |        |         |          |                          |
| Raffinate solution              | 172385.0 | 507.01  | 21125.42 | 74.95                    |
| a) Raffinate                    | 124200.0 | 365.29  | 15220.42 | 54.00                    |
| b) N-methylpyrrolidone          | 48185.0  | 141.72  | 5905.0   | 20.95                    |
| Extraction solution             | 516488.0 | 1519.08 | 63295    | 224.56                   |
| a) Extract                      | 104673.0 | 307.86  | 12827.5  | 45.51                    |
| b) N-methylpyrrolidone          | 411815.0 | 1211.22 | 50467.5  | 179.05                   |
| Losses                         | 1127.0   | 3.31    | 137.92   | 0.49                     |
| Total                          | 690000.0 | 2029.41 | 84558.75 | 300.00                   |
2.2. Heat balance of the extraction column

Amount of heat brought to the column by the streams, kJ/hour:

\[ Q_1 = g_C \cdot I_C^{60} + g_{NMP} \cdot I_{NMP}^{80}, \]

where \( I_{NMP}^{80} \) is N-methylpyrrolidone enthalpy at the temperature of 80 °C, \( g_{NMP} \) N-methylpyrrolidone, kg/hour [16-18].

\( I_C^{60} \) is the distillate enthalpy at the temperature of 60 º C, kJ/kg.

\[ I^t = \frac{4.187}{\sqrt{\frac{15}{\rho}}} \left( 0.403 \cdot t + 0.000405 \cdot t^2 \right), \]

\[ \rho_{15}^{15} = \rho_{4}^{20} + 5 \cdot \alpha, \]

where \( \alpha \) is the density correction, [5].

\[ Q_1 = 56372.5 \cdot 143.49 + 28186.25 \cdot 112.02 = 11.24 \cdot 10^6 \text{ kJ/hour} \]

We have determined enthalpies of the products produced at the temperatures stated and defined the amount of heat taken from the column, kJ/hour:

\[ Q_2 = g_{raf} \cdot I_{raf}^{80} + g_{NMP} \cdot I_{NMP}^{80} + g_e \cdot I_e^{65} + g_{NMP} \cdot I_{NMP}^{65} \]

\[ Q_2 = 50467.5 \cdot 114.96 + 12827.5 \cdot 118.33 + 5905.0 \cdot 143.49 + 15220.42 \cdot 156.09 = 10.54 \cdot 10^6 \text{ kJ/hour} \]

\( Q_1 \approx Q_2. \)

2.3. Structural dimensions of the extraction column

Column diameter:

\[ D_c = \sqrt{\frac{4 \cdot F}{\pi}}; \]

\[ F = \frac{V_{mx}}{\omega}, \]

where \( V_{mx} \) is the mixture volume, m³/hour; \( \omega \) is the speed of streams, m³/m²·hour; taken as 14 m³/m²·hour.

\[ V_{mx} = V_{NMP} + V_F \]

where \( V_{NMP} \) is the volume of N-methylpyrrolidone, m³/hour; \( V_F \) is the feedstock volume, m³/hour.

\[ V_{NMP} = \frac{G_{NMP}}{\rho_{NMP}}, V_C = \frac{G_C}{\rho_C}, \]

where \( G_{NMP}, \rho_{NMP} \) are the bulk quantity and density of the extraction solution; \( G_C, \rho_C \) are the bulk quantity and density of the raffinate solution.

\[ D_c = \sqrt{\frac{4 \cdot 6.32}{3.14}} = 2.84 \text{ m.} \]

The standard diameter of 2.9 m is taken. Operating height of the extraction column:

\[ H_p = h_1 + h_2 + h_3, \]

where \( h_1 \) is the height of the top settling area, \( h_2 \) is the height of the bottom settling area, \( h_3 \) is the height of the extraction area.

The heights of the top and the bottom settling areas are defined on the basis of the solutions residence time in the settling areas. The following values are assumed: \( \tau_1 = 60 \text{ min} \) for the raffinate solution and \( \tau_2 = 30 \text{ min} \) for the extraction solution.

\[ h_1 = \frac{V_{raf} \cdot \tau_1}{F}, h_2 = \frac{V_{e} \cdot \tau_2}{F}. \]

Six grate bars (raschig rings) are located in the extraction column. The height occupied by trays:

\[ h_3 = n^s \cdot s + (n-l) \cdot s_2, \]

where \( n \) is the number of grid trays, \( n=6; s \) is the height of a packing bed, \( l = 1.2 \text{ m}; s_2 \) is the distance between the packing beds, \( s_2 = 1.2 \text{ m.} \)

Operational height of the column:
\[ H_{op} = 4.26 + 6.12 + 13.2 = 23.58 \text{ m}. \]

3. Calculation for the flash column

Flash column is designed to remove the bulk of solvent from the raffinate solution. The solvent is flashed off at elevated temperatures (up to 280-300 °C) to increase the degree of separation of components [19, 20].

The temperature of the top is selected so as to ensure small residual solvent concentration in the rest of the column - not more than 5% (wt.)

3.1. Material and heat balance of the flash column

**Table 3. Material balance of the flash column.**

| Component         | Quantity, kg/h | Mass % |
|-------------------|----------------|--------|
| Input             |                |        |
| Raffinate solution| 21125.42       | 100    |
| a) Raffinate      | 15220.42       | 72.04  |
| b) NMP            | 5905.0         | 27.96  |
| Total             | 21125.42       | 100    |
| Consumption       |                |        |
| 1. Residue        | 15854.28       | 100    |
| a) Raffinate      | 15220.42       | 96     |
| b) NMP            | 633.86         | 4      |
| 2. NMP distillate | 5271.14        |        |
| Total             | 21125.42       |        |

**Table 4. Heat balance of the flash column.**

| Component         | Quantity, kg/h | t, °C | I, kJ/kg | Q, kJ/h·10⁶ |
|-------------------|----------------|-------|----------|-------------|
| Input             |                |       |          |             |
| Raffinate solution| 21125.42       | 280   | 647.95   | 9.86        |
| a) Raffinate      | 15220.42       | 280   | 998      | 5.26        |
| b) NMP (vapour)   | 5271.14        | 280   | 700      | 0.44        |
| c) NMP (liquid)   | 633.86         | 280   |          |             |
| Total             | 21125.42       |       |          | 15.56       |
| Consumption       |                |       |          |             |
| 1. Residue        | 15854.28       | 270   | 619.91   | 9.44        |
| a) Raffinate      | 15220.42       | 270   | 670      | 0.44        |
| b) NMP            | 633.86         | 270   | 978      | 5.16        |
| 2. NMP distillate | 5271.14        | 166.5 |          |             |
| Total             | 21125.42       |       |          | 15.04       |

3.2. Basic dimensions of the flash column

Column diameter calculation:

\[
D = 1.128 \sqrt{\frac{V_c}{\omega_{all}}} = 1.128 \sqrt{\frac{1.29}{0.9}} = 1.35 \text{ m},
\]

where \(V_c\) is the amount of vapour coming through the most loaded column section (section over the top tray); \(\omega_{all}\) is the allowable vapour rate in the calculated column diameter.

The column diameter of 1.4 m is taken according to GOST 26-02-1401-76.

Operating height of the column flash part is determined as:

\[ H = h_1 + h_2 + h_3, \]

where \(h_1\) is the distance from the upper bottom to the first tray, m; \(h_2\) is the height of the evaporation area, m; \(h_3\) is the liquid bed depth at the bottom of the section, m.
H = 0.7 + 2.8 + 2.0 = 5.5 m.

4. Steam-stripping column model

Solvent content in the raffinate downstream of the column is assumed to be \( x = 0.005 \) mass %. The amount of vapour going to the column is assumed to be \( z = 5 \) mass % of the raffinate solution. Pressure at the top of the column is assumed to be \( P_{\text{top}} = 0.007 \) Mpa.

4.1. Material and heat balance of the steam-stripping column

| Table 5. Material balance of the steam-stripping column. |
|---------------------------------------------------------|
| Component                  | Quantity, kg/h | Mass % |
|---------------------------|----------------|--------|
| Input                     |                |        |
| Raffinate solution        | 15854.28       | 95.24  |
| a) Raffinate              | 15220.42       | 91.43  |
| b) NMP                    | 633.86         | 3.81   |
| 2. Steam                  | 792.714        | 4.76   |
| Total                     | 16646.994      | 100    |
| Consumption               |                |        |
| 1. Liquid phase            | 15221.18       | 91.43  |
| a) Raffinate              | 15221.18       | 91.43  |
| 2. Vapour phase            | 1425.814       | 8.56   |
| a) NMP                    | 633.1          | 3.80   |
| b) Steam                  | 792.714        | 4.76   |
| Total                     | 16646.994      | 100    |

| Table 6. Heat balance of the steam-stripping column. |
|------------------------------------------------------|
| Component                  | Quantity, kg/h | t, °C | I, kJ/kg | Q, kJ/h·10^6 |
|---------------------------|----------------|-------|---------|--------------|
| Input                     |                |       |         |              |
| Raffinate solution        | 15854.28       |       |         | 11.61        |
| a) Raffinate              | 15220.42       | 260   | 592.23  | 9.01         |
| b) NMP (liquid)           | 633.86         | 260   | 635     | 0.4          |
| Steam                     | 792.714        | 180   | 2778    | 2.2          |
| Total                     | 16646.994      |       |         | 11.61        |
| Consumption               |                |       |         |              |
| 1. Residue (raffinate)    | 15221.18       | 252   | 570.35  | 8.68         |
| 2. Distillate             | 1425.814       |       |         | 2.65         |
| a) NMP                    | 633.1          | 76    | 883     | 0.56         |
| b) Steam                  | 792.714        | 76    | 2645    | 2.09         |
| Total                     | 16646.994      |       |         | 11.33        |

4.2. Basic dimensions of the steam-stripping column

Column diameter calculation:

\[
D = 1.128 \sqrt[\omega_{\text{all}}]{\frac{V_C}{\omega_{\text{all}}} = 1.128 \frac{6.13}{3.76} = 1.44 \text{ m}},
\]

The column diameter of 1.5 m is taken according to GOST 26-02-1401-76. Operating height of the steam-stripping column is determined as:

\[
H = h_1 + h_2 + h_3 + h_4 + h_5,
\]
where \( h_1 \) is the height to the first tray, m; \( h_2 \) is the height of the stripping area, m; \( h_3 \) is the liquid bed depth at the bottom of the section, m; \( h_4 \) is the height of the column bottom, m; \( h_5 \) is the height of the column substructure, m.

Thus \( H = 0.75 + 2.8 + 1 + 1.01 + 2 = 7.56 \) m

5. Calculation for the furnace
The furnace is designed for the heating of raffinate solution up to the temperature \( t_2 = 285^\circ C \). The initial feedstock temperature (downstream of the heat exchanger) is \( t_1 = 200^\circ C \).

The heating area of radiant tubes is defined according to the formula:

\[
H_r = \frac{Q_r}{q_r} = \frac{5.27 \times 10^6}{40600} = 130 \text{ m}^2 ,
\]

where \( Q_r \) is the amount of heat transferred to the feedstock in the radiant chamber, kW, \( q_r \) is the heat liberation rate of radiant tubes, kW/m².

The tubes with the diameter of 127 mm and the effective length of \( l_{tu} = 10 \) m are chosen.

The number of radiant tubes:

\[
N_r = \frac{H_r \pi \cdot d_h \cdot l_{tu}}{3.14 \cdot 0.127 \cdot 10} = 33
\]

The heating surface of convection tubes is defined according to the formula:

\[
H_c = \frac{Q_c}{k_1 \Delta T_m},
\]

where \( Q_c \) is the amount of heat transferred to the feedstock in the convection tubes, W; \( k_1 = 32.6 \) is the heat-transmission coefficient in the furnace convection section, W/(m²K); \( \Delta T_m \) is the mean temperature difference, K.

We can calculate the stream enthalpy downstream of the convection section \( J_r \):

\[
J_r = J_{200} + \Delta J_c,
\]

where \( J_{200} \) is the stream enthalpy upstream of furnace, kJ/kg; \( \Delta J_c \) is the stream enthalpy transferred in the convection section kJ/kg.

\[
J_r = 446.70 + 118.88 = 565.58 \text{ kJ/kg}.
\]

We have plotted a diagram of variation of enthalpy in relation to temperature and used this dependency to determine the temperature of entry to the radiant chamber when the enthalpy is known to be \( J = 565.58 \) kJ/kg. The temperature of entry to the radiant chamber is \( t_c = 251^\circ C \).

In the convection chamber the heat is transferred from the flue gases to the feedstock in the tubes by a mixed-cross current with a countercurrent index equal to one. Therefore, the mean temperature difference is calculated by the Grashof’s equation:

\[
\Delta T_m = \frac{\Delta T_{max} - \Delta T_{min}}{\ln \frac{T_{max}}{T_{min}}}
\]

where \( \Delta T_{max} = T_p - T_c = 750 - 251 = 499 \),

\[
\Delta T_{min} = T_{yx} - T_1 = 320 - 200 = 120.
\]

\[
\Delta T_m = \frac{499 - 120}{\ln \frac{499}{120}} = 266
\]

Thus, the heating surface of convection tubes is estimated at

\[
H_c = \frac{1.22 \times 10^6}{32.6 \cdot 266} = 141 \text{ m}^2.
\]

The tubes with the effective length of \( l_{tu} = 10 \) m and the outer diameter of 102 mm are installed in the convection chamber.

The number of tubes in the convection chamber is estimated at:

\[
N_c = \frac{H_c}{\pi \cdot d_c \cdot l_{tu}} = \frac{141}{3.14 \cdot 0.102 \cdot 10} = 44
\]

Based on the data obtained, one furnace of the type TC-2 156/10 was chosen.
6. Calculation for the heat exchanger

The purpose of calculations for the heat exchanger is to determine the heat exchange surface and to select the appropriate size and type of the device. We can calculate the heat exchanger properties needed to heat the raffinate solution up to 200 °C. The raffinate enters the heat exchanger at a temperature $t_1 = 252 ^\circ C$ and goes out at a temperature $t_2 = 120 ^\circ C$. The efficiency of the heat exchanger is assumed to be $\eta = 0.96$.

Let us put down the heat balance equation:

$$ Q_1 = G_{sol} \cdot \left( \frac{252}{raf} - \frac{120}{raf} \right), $$

The heat from the hot stream:

$$ Q_1 = 13725.00 \cdot (1094.67 - 242.85) - 11.69 \cdot 10^6 \text{ kJ}. $$

We have determined the mean difference of heating medium temperatures taking into account the counter-current of heating mediums in the device according to the scheme:

80 °C $\longrightarrow$ 200 °C (raffinate solution)

120 °C $\longleftrightarrow$ 252 °C (raffinate)

$\Delta t_{\text{max}} = 40 ^\circ C$, $\Delta t_{\text{min}} = 52 ^\circ C$.

Since $\Delta t_{\text{max}} / \Delta t_{\text{min}} < 2$, $\Delta t_m$ is defined according to the formula:

$$ \Delta t_m = \frac{\Delta t_{\text{max}} + \Delta t_{\text{min}}}{2} = \frac{40 + 52}{2} = 46 ^\circ C. $$

The heat-transmission coefficient in the heat exchanger is assumed from the practical data $k = 280 \text{ kJ/(m}^2\cdot\text{h} \cdot \text{degr)}$. Thus, the heat exchange surface will be calculated according to the formula:

$$ F = \frac{Q_1}{k \cdot \Delta t_m} = \frac{11.69 \cdot 10^6}{280 \cdot 46} = 907.61 \text{ (m}^2). $$

We have chosen 2 tube-and-shell floating-head heat exchangers with the heat exchange surface of 460 m², the tubes length is 6000 mm, shell diameter is 1200 mm, tubes diameter is 25 mm, number of tube-side passes is 4.

7. Conclusion

We have developed a project of a solvent refining plant using the N-methylpyrrolidone solvent. We have calculated the material and heat balances of the process, main and auxiliary equipment: tube furnace, heat exchangers, extraction and regeneration columns.

8. References

[1] Starovoitova N 2002 Automotive engine oils World of Oil Products 1 p 23
[2] Lastovkin G, Radchenko E D and Rudin M G 1986 Handbook of the Petroleum Refiner (Leningrad: Chemistry) p 648
[3] Akhmetov S 2002 Technology of deep oil and gas processing (Ufa: Publishing House “Gilem”) p 671
[4] Nigmatullin R, Zolotarev P, Saiullin N, Telyashchev G and Medzhibovsky A 1998 Selective Treatment of crude oil (Moscow: Oil and gas) p 208
[5] Kazakova L and Krein S 1978 Physicochemical production of petroleum oils (Moscow: Chemistry) p 320
[6] Mazzanti U and Frempton L 1976 Furfural cleaning in oil salvage Hydrocarbon processing 8 pp 17–28
[7] Kozh A and Zubovich V 2006 Chemistry and Technology of Fuels and Oils 3 p 12
[8] Bogdanov N 1970 Chemistry and Technology of Fuels and Oils 3 pp 42–50
[9] Marushkina V 1980 Research to improve the refinement technology of mineral oils: Abstract of the dissertation for academic degree of candidate of technical sciences (Ufa) p 24
[10] Kolesnik I 2003 The process of selective treatment of crude oil with N-methylpyrrolidone Chemistry and Technology of Fuels and Oils 2 p 4
[11] Akhmetov S, Kuzeev I and Baziyatov M 2006 Technology and equipment for oil and gas processing Study guide (St. Petersburg: Nedra) p 868
[12] Kalekin V 2004 *Machines and devices of chemical production* (Omsk: Publishing House of Omsk State Technical University) p 344
[13] Samedova F and Gasanova R 2013 Increasing the efficiency of selective treatment of viscous distillate by various solvents *World of Oil Products* 4 p 7
[14] Mukhametova R and Nigmatullin V 2006 *Oil and gas engineering* 4 pp 39–41
[15] Fuks I and Sovchenko T 2005 Improvement and intensification of technological processes of the production of lubricating oils and solid hydrocarbons *Oil, gas and business* 2-3 pp 73–80
[16] Belyaev A, Gribenik T and Kotov A 2011 *World of Oil Products* 1 pp 38–42
[17] Bernalson M, Tatur I and Tonkonosov B 2011 *Chemistry and Technology of Fuels and Oils* 1 pp 16–18
[18] Rabzhad M and Ledenev S 2013 Analysis of the plant for selective treatment of oils with phenol *Modern high technologies* 2 pp 110–111
[19] Babkina A, Chzhen V and Anishchenko O 2010 Improvement of the process of selective treatment of oils with phenol *Modern high technologies* 4 p 106
[20] Izibaeva A, Kondrasheva I and Kondrashev D 2010 Improvement of the technology of production of basic mineral oils *Bashkir chemical journal* 17(2) pp 82–85