DOI 10.1007/s10553-022-01410-7
Chemistry and Technology of Fuels and Oils, Vol. 58, No.3, July, 2022 (Russian Original No.3, May – June, 2022)

INNOVATIVE TECHNOLOGIES OF OIL AND GAS

SLACK WAX DEOILING BY STATIC CRYSTALLIZATION

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The possibility of producing semi-purified and deeply deoiled paraffins from slack waxes by the method of static crystallization is investigated. Optimal parameters of a one-stage deoiling process for obtaining semi-purified paraffins with an oil content of less than 3 wt% were determined. The potential of a two-stage deoiling process for production of deeply deoiled paraffins with an oil content of less than 1 wt% was demonstrated. The economic efficiency of the proposed methodology of slack wax deoiling by static crystallization was confirmed by calculations.

Keywords: oil solid paraffins, slack wax deoiling by thermal methods, static crystallization.

The world output of oil paraffins as of 2020 amounted to 3293 thousand tons [1]. Over the past decade, however, this value has remained at the same level, largely due to a decrease in the demand for group I base oils, whose manufacturing involves the formation of oil paraffins as by-products. The cost efficiency of obtaining group I base oils in an average refinery plant is rather low and is expected to decrease further with the development of production facilities for processing vacuum gas oil into light oil products [2]. The main trend has so far been a reduction in the production of unrefined paraffin waxes in North America and Europe as a result of employing feedstock slack wax in the production of group II and III base oils. Another significant factor in this process consists in the introduction of stricter environmental regulations on combustion products and subsequent adoption of the RAL-GZ-041 quality assurance standard [3], which restricts the use of crude and semi-purified paraffins in the production of candles for domestic use. China, whose share in the total production of oil paraffins amounts to about 50%, is likely to be capable of meeting the demand for paraffine products in the future (**Fig. 1**). However, taking into account transportation costs, their selling price will be higher in comparison with paraffins produced in the EU.

In the long term, the demand for oil paraffins is expected to undergo structural transformations, with the focus shifting toward deeply deoiled and refined paraffins. This trend is supported by environmental initiatives aimed at expanding the use of

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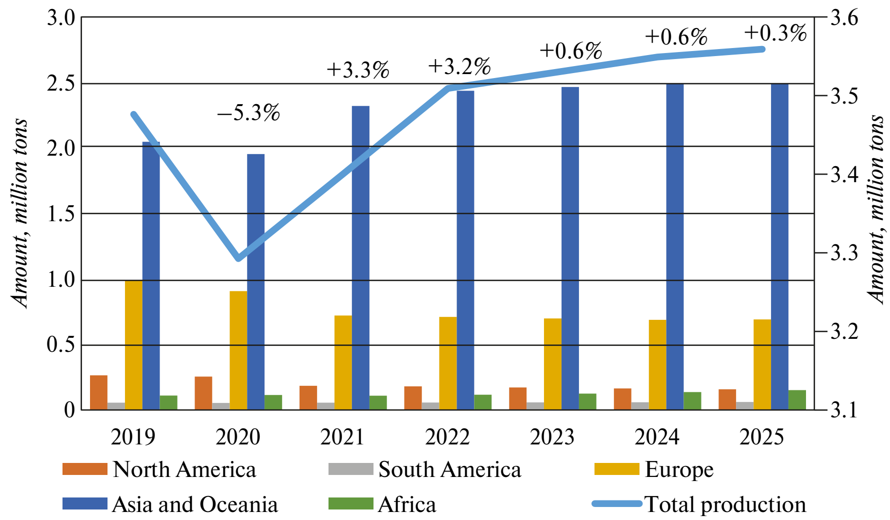

Fig. 1. Oil paraffine production forecast by regions of the world

paper-based packaging materials, whose production require oil paraffines [4]; an increase in the consumption of oil paraffins in the cosmetic industry [5], particularly for the production of personal hygiene products; an increase in the market for candles and candle compositions [6].

The low economic efficiency of producing group I base oils can be overcome by the output of high-quality paraffin wax products. In comparison with foreign manufacturers offering a diverse range of oil paraffins of different quality and properties, Russian companies produce mainly unrefined oil paraffins and slack waxes of various distillation levels. In order to bridge this gap, new approaches to processing paraffin-containing raw materials should be developed and the existing deoiling installations should be upgraded. Another restricting factor is the dependence of Russian refineries on the import of methyl ethyl ketone (MEK), a compound used as a solvent in the production process. More than 90% of MEK is supplied from abroad, mainly from the Asian region [7, 8].

At present, thermal deoiling methods requiring no solvents are gaining in popularity. The implementation of such methods intensified in the 2000s in connection with the tightening requirements for environmentally friendly products and industries [9]. For example, Sulzer Chemtech has patented a technology referred to as static crystallization, which involves a crystallization of paraffin in the form of large crystals during a slow cooling of molten slack wax under a temperature below its melting point by 10–20°C. The oil contained in the starting material is thereby distributed in the bulk and on the surface of the paraffin. The remaining liquid phase is drained by gravitational forces during the subsequent stages of heating and holding. This method can be used to obtain not only paraffins with a low oil content (**Table 1**), but also to fractionate them according to melting points at a certain temperature regime.

The method of static crystallization possesses significant advantages over that of deoiling with ketone-aromatic solvents, including lower production costs (the process is carried out in the temperature range of 20–80°C, no units for crystallization and vacuum creation are required), low environmental impact (no toxic solvents, closed circulation of the coolant), as well as no dependence on imported solvents.

Table 1

Parameter	Slack wax sample No.			
	1	2	3	4
Feedstock				
Melting point, °C	46.0	47.0	44.0	51.0
Paraffin content, wt%	71.0	72.0	69.0	98.0
Paraffin				
Melting point, °C	51.0	52.0	52.0	54.0
Oil content, wt%	4.6	2.3	0.9	0.5
Paraffin yield, wt% per starting materials	39.0	26.0	20.0	31.0

Table 2

Parameter	Analysis method	Slack wax sample No.	
		1	2
Kinematic viscosity at 100°C, mm^2/sec	ASTM D 445	3.905	3.851
Density at 20°C, g/cm^3	ASTM D 4052	0.847	0.855
Melting point, °C	ASTM D 87	52.1	44.3
Oil content, wt%	ASTM D 721	6.52	28.54
Sulfur content, wt%	ASTM D 4294	0.052	0.114
Flash point in an open crucible, °C	ASTM D 92	218	212
Water content, wt%	ASTM D95	Absent	Absent
Content of mechanical impurities, %	ASTM D 4807	Absent	Absent
Boiling range, °C	ASTM D 2887	330–480	350–485
Content of components boiling over 470°C	ASTM D 2887	3.7	4.1

The most preferred raw materials for production of high-quality paraffines by static crystallization include slack waxes with a high concentration of normal alkanes with a carbon atom number of 24–30 and their total content of more than 30%. The deoiling of slack waxes with a C_{35}+ hydrocarbon content of over 15% leads to a decrease in the overall economic efficiency [10, 11].

In this paper, we investigate the deoiling of industrial slack waxes at a laboratory static crystallization unit with a volume of 350 ml. The temperature regime was maintained automatically using a thermostat equipped with a programmable control unit. In order to increase the efficiency of oil removal, as well as to prevent its solidification in the branch pipes, the lower part of the crystallizer was equipped with an additional heating system.

Two samples of slack wax were used as starting materials, characterized by approximately the same viscosity of 3.8–3.9 mm^2/sec but differing in the melting point and oil content (**Table 2**). The increased oil content in sample *2* was associated with a higher sulfur content. The determined fractional composition of the studied slack wax samples showed the content of components boiling above 470°C to be less than 5 wt%. This indicates an insignificant presence of hydrocarbons that contribute to the formation of a fine-crystalline structure incapable of releasing a liquid phase when heated [12]. On this basis, the slack waxes selected for our research were considered to be a favorable starting material for deoiling using a thermal method.

In total, 28 experiments were conducted at different temperatures to determine 14 optimal process parameters for each slack wax sample. The main criterion for selecting temperature regimes was the residual oil content in the final product, which was found to be less than 3 and 5 wt% for samples *1* and *2*, respectively. For each slack wax type, the effect of the final cooling temperature and cooling rate, as well as that of the final heating temperature and heating rate, on the physicochemical properties and yield of the resulting paraffins was studied.

An analysis of the data obtained during the crystallization stage showed the need to use the final cooling temperature of at least 15°C below the melting point for both slack wax samples in order to avoid an undesirable collapse of the slack wax column into paraffin. The low deformation stability of slack wax in the selected temperature range is explained by the occurrence of phase transitions and, hence, by different characteristics of crystalline structures in high- and low-temperature regions. Upon a further increase in the difference between the melting point of slack wax and the final cooling temperature, an increase in the yield of paraffins with a lower oil content was observed.

The cooling rate is another significant factor affecting the formation of crystalline structures. An optimal cooling rate was found to be 6 deg/h. The use of lower cooling rates causes an increase in the duration of the process, thereby deteriorating the performance of the installation without significant improvements in the paraffin quality.

The heating rate was found to be a limiting process parameter. Thus, a decrease in the heating rate from 1 to 0.5 deg/h leads to a two-fold increase in the process duration, which has a significant impact on its technical and economic indicators. An optimal heating rate varies from 1 to 1.5 deg/h, allowing paraffins with an oil content of less than 3 wt% to be obtained. When producing paraffins with an oil content of less than 5 wt%, the heating rate may have to be increased to 2 deg/h. This may contribute to obtaining products with a reduced giveaway gap.

In comparison with other process parameters, the final heating temperature was established to have the greatest impact on the

Table 3

Parameter	Paraffine				
	Slack wax 1			Slack wax 2	
Mode No.	1	2	3	4	5
Yield, wt%	78.6	82.1	65.1	19.9	42.9
Process duration, h	11.5	11.2	16.8	27.7	14.8
Oil content, wt%	1.79	2.89	1.34	1.71	3.91
Melting point, °C	55.0	54.9	56.9	55.8	53.5
Kinematic viscosity at 100°C, mm^2/sec	3.951	3.936	4.089	3.907	3.886
Density at 20°C, g/cm^3	0.839	0.849	0.865	0.888	0.875
Sulfur content, wt%	0.029	0.031	0.021	0.048	0.075
Flash point in an open crucible, °C	228	234	240	236	230

quality and yield of paraffins. By varying this parameter across the range from 47 to 56°C, paraffins of different melting points and residual oil contents can be obtained, as demonstrated by **Table 3**.

The dependence of the paraffin yield on the final heating temperature was found to follow exponential law. Thus, upon its increase, a sharp decrease in the paraffin yield was observed. At the same time, the content of residual oil grows not as sharply, following a linear dependence.

Table 3 shows that, compared to the starting compositions, all paraffin samples are characterized by increased values of such indicators as flash point, kinematic viscosity, and melting point. This can be explained by the slack wax extraction process yielding not only oil components, but also low-melting solid hydrocarbons with lower values of the noted indicators.

Table 4 presents optimal temperature regimes for one-stage slack wax deoiling to obtain paraffins of technical grades.

In order to confirm the possibility of producing paraffins with an oil content of less than 1wt%, samples obtained during the deoiling of slack waxes *1* and *2* under modes *1*, *2*, and *5*, respectively, were subjected to a second stage of deoiling under temperature holding during heating. Table 5 presents the characteristics of paraffins obtained through the two-stage deoiling of slack waxes.

According to the main quality indicators, paraffins obtained at regimes *6–8* correspond to deeply deoiled grades thus representing a potential raw material for the production of highly refined paraffins used in the production of packaging materials and

Table 4

Parameter	Slack wax 1			Slack wax 2	
	1	2	3	4	5
Cooling stage					
Initial temperature, °C	58	58	58	52	52
Thermostating duration, h	2.7	3.0	3.3	3.2	2.6
Final temperature, °C	42	40	38	33	36
Cooling rate, deg/h	6.0	6.0	6.0	6.0	6.0
Holding stage					
Initial temperature, °C	42	40	38	33	36
Thermostating duration, h	0.5	0.5	0.5	0.5	0.5
Final temperature, °C	42	40	38	33	36
Heating stage					
Initial temperature, °C	42	40	38	33	36
Thermostating duration, h	7.3	6.7	12.0	23.0	10.7
Final temperature, °C	53	50	56	56	52
Heating rate, deg/h	1.5	1.5	1.5	1.0	1.5
Paraffine melting stage					
Initial temperature, °C	53	50	56	56	52
Thermostating duration, h	1.0	1.0	1.0	1.0	1.0
Final temperature, °C	80	80	80	80	80
Heating rate, deg/h	60	60	60	60	60
Total duration, h	11.5	11.2	16.8	27.7	14.8

Table 5

Parameter	2nd stage paraffine		
	Slack wax 1		Slack wax 2
Mode No.	6	7	8
Total yield, wt%	46,9	50,2	18,0
2nd stage yield, wt%	59,7	61,2	42,0
2nd stage duration, h	16,5	13,5	19,5
Total duration, h	28,0	24,7	34,3
Oil content, wt%	0,44	0,58	0,75
Melting point, °C	57,2	57,0	56,8

cosmetics. The deoiling of slack waxes with an oil content of more than 20 wt%, a two-stage method seems more expedient, as demonstrated by Tables 3 and 5. Thus, when processing slack wax *2* in two stages (mode *8*), a paraffin with a lower residual oil content and a yield comparable to that obtained via a one-stage process (mode *4*) is produced.

The economic efficiency of implementing static crystallization in the production of paraffins and paraffin-wax products was calculated on the example of a Russian refinery plant [13]. The calculated economic efficiency indicators of the process of obtaining paraffins with an oil content of less than 0.5 wt% were found to be as follows: net present value (NPV) – 926 million rubles, internal annual rate of return (IRR) – 57.3%, and profitability index (PI) – 4.49. It should be noted that the efficiency of a project is frequently estimated based on the threshold IRR value of at least 25%.

It can be concluded that, taking into account the growing interest in thermal deoiling processes and demand for deeply deoiled products, static crystallization is a highly promising technology for processing low- and medium-boiling slack waxes. The conducted studies have confirmed its prospects for producing marketable semi-purified paraffines with an oil content of less than 3 wt%. The potential of the two-stage deoiling process for obtaining deeply deoiled paraffines with a medium and high oil content was demonstrated. Economic calculations confirmed the expedience of implementing the method of static crystallization at refinery plants.

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