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An Experimental Study on the Operational Factors Affecting the Oil Content of Wax during Dewaxing Process: Adopting a DOE Method

M. H. Eghbali, A. R. Solaimany Nazar*, and T. Tavakoli

Department of Chemical Engineering, University of Isfahan, Isfahan, Iran

Abstract

The oil content of the wax produced in a dewaxing process is the key economic parameter that should be reduced as much as possible. Some factors such as the type of solvents, cooling rate, temperature, and solvent to oil ratio influence the dewaxing process. Due to the fact that crude oil differs from place to place and since the operational conditions for wax extraction vary for different types of crude oil, the objective of this work is to study the operational conditions for wax production from an Iranian raffinate sample used in Sepahan Oil Company. All the experiments are conducted based on a design of experiment (DOE) technique for minimizing the oil content of the wax produced. The effects of five factors have been determined quantitatively and appropriate levels are suggested for reducing the oil content. The results show that the solvent ratio, solvent composition, and cooling rate play the most important role in minimizing the oil content of the produced wax.

Keywords: Oil Content, Wax, Dewaxing Process, Design of Experiment

1. Introduction

Paraffinic wax of petroleum mixtures can precipitate when temperature decreases during oil production through a dewaxing process. The storage of waxy crude stream is difficult as it produces a great amount of gel and sludge in the storage tank. This phenomenon leads to a raise in pumping expenses and cleaning costs. If this wax is removed, the problems of accumulation in storage tanks and the piping system corrosion will be minimized (Visintin et al., 2008; Doctor et al., 2003). The use of solvents for the separation of oil and wax for the production of superior wax-free lubricating oils from paraffin-based crudes has been discussed by a number of investigators (Larikov et al., 1977). In dewaxing processes, the principal solvents are benzene, methyl ethyl ketone (MEK), methyl isobutyl ketone, propane, petroleum naphtha, ethylene dichloride, methylene chloride, sulfur dioxide, and N-methyl pyrrolidinone. In solvent dewaxing processes, the oil is first diluted with a solvent that has a high affinity for oil, and it is then chilled to precipitate the wax; it is next filtered to remove the wax and is stripped of the solvent; finally, it is dried. The solvents (mainly propane, naphtha, and MEK) act as diluents for the high molecular weight oil fractions in order to reduce the viscosity of the mixture and provide sufficient liquid volume to permit pumping and filtering. The wax produced by the solvent dewaxing process is used for candle wax, cosmetics micro wax, and petroleum jelly wax production (Wauquier, 2000). The two different methods for wax removal are the solvent and catalytic methods. Dewaxing of crude oils using diverse methods to separate wax and oil such as dewaxing

* Corresponding Author:
Email: asolaimany@eng.ui.ac.ir

with nonporous membranes, extraction and adsorption of waste lubricating oils, supercritical extraction for the production of biodiesels, solvent dewaxing, and catalytic dewaxing to decrease the solid point of the dewaxed oil has been studied by several investigators (Manjula, 2009; Mohammad et al., 2013). The competition between traditional solvent and hydrocatalytic dewaxing methods will continue in the near future. However, traditional technologies will probably outperform hydrocatalytic processes in the foreseeable future because of the fact that using traditional solvent dewaxing methods will result in the production of petroleum waxes, ultrahigh-index group III oils, and group II oils. Besides, the power consumption and consequently the atmospheric emissions of combustion products are higher in hydrocatalytic dewaxing methods (Vishnevskii, 2007).

Solvent dewaxing is more selective for removing both heavy normal and non-normal hydrocarbons. Nevertheless, catalytic dewaxing removes the normal paraffin more evenly over the boiling range, while the light non-normal hydrocarbons are removed more selectively. The oil obtained from solvent dewaxing has a higher yield and viscosity index than that of the catalytic dewaxing (Thanh et al., 1999; Taylor et al., 1992). The oil content of the wax is one of the most economic parameters in a dewaxing unit and must be reduced as much as possible. Some operational factors such as the type of the solvents, cooling rate, temperature, and solvent to oil ratio influence the dewaxing process (Zolotarev et al., 1997).

Due to the fact that crude oil differs from place to place and since the operational conditions for wax extraction vary for different types of crude, the objective of the present work is to study the operational conditions for wax production from an Iranian raffinate used in Sepahan Oil Company of Isfahan. In this study, the influences of solvent composition, solvent to oil ratio, cooling rate, solvent type, and crystallization temperature on wax extraction are investigated. All the experiments are conducted by using design of experiments (DOE) as a statistical method for studying the important parameters affecting a certain target.

2. Experimental

2.1. Materials

An Iranian raffinate sample of the Sepahan Oil Company of Isfahan, the properties of which is given in Table 1, is used as the feed for dewaxing process. The vacuum distillation analysis of the raffinate is given in Table 2. The data are measured based on ASTM D1160 standard and the model of the apparatus used is Herzog HDV632. The density of the raffinate is 830 kg/m^3 at 60 °C.

Four solvents, namely MEK, toluene, MTBE and acetone, are used in this study. Acetone is supplied by Merck Company with a purity of 99.9% and MTBE is prepared from Mahshahr Petroleum Refinery with a purity of 99%.

Table 1
Properties of the waxy crude oil sample

Property	Value
Boiling range (°C)	440-530
Viscosity index	90
Pour point (°C)	45
Wax content (%)	36

Table 2
Results of raffinate vacuum distillation

Volume distilled (%)	Distillation rate (ml/min)	Thermo reading (°C)	Operating pressure (mbar)	Atmospheric equivalent temperature (°C)	Liquid temperature (°C)
5	3.8	304.2	29.92	443.1	335.8
10	7.1	312.7	29.42	453.2	340.9
20	5.9	330	29.32	472.4	348.4
30	7.5	337.9	29.52	480.9	353.7
40	7.2	343.8	29.32	487.6	358.3
50	7.5	347.6	29.32	491.8	362.1
60	7.7	351.8	29.92	495.7	366.3
70	6.7	357.9	29.72	502.6	370.9
80	6.9	362	29.32	507.6	375.4
90	5.8	371	29.52	517.2	381.5
95	6.4	375.2	29.62	521.6	385.6
99	6	382.4	29.82	529.2	390.8

2.2. Methods

The experimental procedure of the dewaxing process includes four steps. The waxy crude oil sample is mixed with the solvents and then cooled to crystallize wax components. Next, the mixture is filtered applying a vacuum pump to separate the wax and oil. The recovery of solvents by distillation is the final step. The oil content of the wax is measured through ASTM D721 standard.

2.3. Design of experiments

There are five factors to be considered here. These factors and their coded levels are shown in Table 3. The proper selection of these limits is very important and if they are not chosen correctly all the experimental design and the result evaluation will be affected. The results are analyzed through Minitab 14 software. The method of standard error on the basis of minimizing the oil content of the produced wax is applied. Twenty seven runs of experiments are selected to carry out the dewaxing process with various operational parameters (Table 4). The results are analyzed with the design of experiment technique and the magnitude of their effects is determined. The experiments are conducted with one repetition. For the experiments with repetitions, the signal-to-noise (*S/N*) ratios should always be used in the analyses. The signal-to-noise ratio (*S/N*) is used as a transformed response in the Taguchi method to indicate the magnitude of changes in response due to the variations of controlled factors with respect to that of the errors. As mentioned above, the results of oil content were used in the response analysis. In order to minimize the oil content, the following *S/N* equation is used (Roy, 2001):

$$S/N = -10\log_{10}\left(\frac{y_1^1 + y_2^2 + \ldots + y_n^2}{n}\right) \tag{1}$$

where, y is the experimental measurement of the oil content, and n stands for the number of repetitions, which is equal to 2 in this work.

Table 3
Factors and their corresponding levels for screening experiments

Factors	Unit	Level 1	Level 2	Level 3
Crystallization temperature	°C	-15	-20	-25
Solvent ratio	-	2	3	4
Solvent type	-	MEK:Toluene	MIBK:Acetone	MTBE:Acetone
Solvent composition	-	1:1	2:1	3:1
Cooling rate	°C/min	3	4	5

Table 4
Levels of the factors and their corresponding oil content for screening experiments

Run	Solvent type	Solvent composition	Solvent ratio	Crystallization temperature (°C)	Cooling rate (°C/min)	Responses		
						Oil content 1 (wt.%)	Oil content 2 (wt.%)	*S/N* Ratio
1	1	1	1	1	1	34	35	-30.7573
2	1	1	2	2	2	20	19	-25.8035
3	1	1	3	3	3	6	6	-15.5630
4	1	2	1	2	3	29	31	-29.5472
5	1	2	2	3	1	27	27	-28.6273
6	1	2	3	1	2	19	18	-25.3466
7	1	3	1	3	2	36	35	-31.0054
8	1	3	2	1	3	28	29	-29.0982
9	1	3	3	2	1	31	32	-29.9673
10	2	1	1	1	1	35	36	-31.0054
11	2	1	2	2	2	21	20	-26.2377
12	2	1	3	3	3	7	7	-16.9020
13	2	2	1	2	3	30	29	-29.3977
14	2	2	2	3	1	28	26	-28.6332
15	2	2	3	1	2	20	18	-25.5871
16	2	3	1	3	2	37	37	-21.3640
17	2	3	2	1	3	29	31	-29.5472
18	2	3	3	2	1	19	20	-25.8035
19	3	1	1	1	1	36	37	-31.2467
20	3	1	2	2	2	22	23	-27.0458
21	3	1	3	3	3	8	8	-18.0618
22	3	2	1	2	3	31	29	-29.5472
23	3	2	2	3	1	29	28	-29.0982
24	3	2	3	1	2	21	21	-26.4444
25	3	3	1	3	2	38	38	-31.5957
26	3	3	2	1	3	30	31	-29.6872
27	3	3	3	2	1	28	27	-28.7881

3. Results and discussion

The oil content measurements corresponding to each experiment run are repeated twice and the results are shown in the last two columns of Table 4. Table 5 shows that solvent ratio is the most important factor with the highest rank in our response (oil content) in a manner that the oil content decreases when the solvent ratio is increased. The other factors and their ranks are also specified in this table. Another important set of data in a DOE analysis is the ANOVA table, which determines the errors and percentage of the contribution of the factors to the response parameter, i.e. oil content herein (Table 6).

Table 5
Factors and their magnitude of effects and ranks

	Solvent type	Solvent composition	Solvent ratio	Cooling rate	Crystallization temperature
Level 1	-27.3	-24.74	-30.61	-29.33	-28.75
Level 2	-27.16	-28.03	-28.20	-27.83	-28.02
Level 3	-27.95	-29.65	-23.61	-25.26	-25.65
Rank	5	2	1	3	3

Table 6
ANOVA table of the factors and their effects of the screening experiments

	DF	Seq SS	Adj SS	Adj MS	F-Ratio	P-Value
Solvent type (dimensionless)	2	17.57	17.57	8.787	2.01	0.196
Solvent composition (dimensionless)	2	431.13	431.13	215.565	49.32	0.000
Solvent ratio (dimensionless)	2	1225.35	1225.35	612.676	140.19	0.000
Crystallization temperature (°C)	2	89.8	89.8	44.898	10.27	0.006
Cooling rate (°C/min)	2	257.19	257.19	128.593	29.42	0.000
Solvent type×Solvent ratio	4	18.7	18.7	4.676	1.07	0.431
Solvent type×Crystallization temperature	4	22.59	22.59	5.648	1.29	0.350
Residual error	8	34.96	34.96	4.37		
Total	26	2097.3				

3.1. Influence of solvent ratio

As indicated above, the most important factor affecting the oil content of wax is solvent ratio which has the highest percentage of contribution. With an increase in the volume of the solvent, the viscosity of the blend decreases; this induces a crystal growth which consequently leads to better filtration, and thereby a decrease in the oil content. The volume of the solvent should not be more than an optimized volume because the cost of the solvent recovery could be too high, thereby increasing the total operational cost.

3.2. Influence of solvent composition

The second important factor influencing the oil content is solvent composition. The data show that an increase in the amount of MEK or MTBE as anti-solvents results in higher oil contents. Although an increase in the proportion of anti-solvent improves the filtration rate, it leads to a drop in yield and the oil content of the wax produced. Therefore, we conclude that the amount of solvent composition should be determined in an economic manner that oil content and filtration rates are optimized. However, the proportion of anti-solvent can only be raised up to a certain point, otherwise phase separation occurs, which makes the filtration part impossible.

3.3. Influence of cooling rate

Cooling rate also affects the dewaxing process significantly. Cooling rate influences crystal shape and size as well as oil content. A slow cooling rate usually promotes the growth of crystals with a multilayer spiral type of morphology, which causes oil occlusions and thus more oil content. On the other hand, a fast cooling rate facilitates the formation of smaller crystals with a tendency to form along an axis shaping needle type crystals, which rapidly clogs the filter cloths and reduces filtration rate. Although these types of crystals decrease filtration rate, they cause the oil content to decrease remarkably. It is also important to prevent thermal shocks during the crystallization operation because they make filtration completely impossible.

3.4. Influence of crystallization temperature

The quantitative effect of crystallization temperature is not as much as the other parameters, although it is still of great importance as an operational parameter in dewaxing. This temperature impacts on the pour point needed for the oil produced, but it has a negligible effect on the oil content of the wax. It should be noted that if the product is cooled down to a temperature lower than that of the crystallization temperature, the crystal size increases dramatically. This modifies the rheological properties of the blend, which leads to the crystal cluster formation; the latter significantly affects the value of oil content and the congeal point of the oil.

3.5. Influence of solvent type

Two pairs of solvents are used herein. The performance of these two pairs is similar for the reduction of wax oil content. This means that we can substitute the traditional solvents of MEK and toluene with the new pair of MTBE and acetone. This substitution depends on the availability and the price of these solvents.

3.6. Optimization of experiment

The factors with significant *F*-ratios are the important factors and are chosen for optimization. These factors are solvent ratio, solvent composition, and cooling rate. The other factors such as crystallization temperature are set at their economic values and they are not considered as important as these three factors. The *F*-ratio of the solvent type is not significant either, which indicates that the performance of the three pairs of the solvents used herein in minimizing the oil content of wax is equivalent; therefore, MIBK and acetone are used for the optimization of the dewaxing process. The new levels and factors for the optimization are shown in Table 7. It is clear that the range of the factors is narrowed to get closer to the desired value obtained in the screening tests; this is commonly used in the design of experiments. For the optimization, three factors and three levels are used in an experimental design with 9 runs. The run data of the optimization and the corresponding responses are given in Table 8. The ANOVA table of the optimization experiments is shown in Table 9. The large values of the *F*-ratios indicate that all the factors are significant and their effects are meaningful.

Table 7

Factors and their corresponding level for the optimization experiments

Factors	Unit	Level 1	Level 2	Level 3
Solvent ratio	-	3.5	4	4.5
Solvent composition	-	50:50	55:45	60:40
Cooling rate	°C/min	4.5	5	5.5

Table 8
Levels of the factors and their corresponding oil content for the optimization experiments

Run	Solvent composition	Solvent ratio	Cooling rate (°C/min)	Oil content (wt.%)
1	1	1	1	34
2	1	2	2	20
3	1	3	3	6
4	2	1	3	29
5	2	2	1	27
6	2	3	2	19
7	3	1	2	36
8	3	2	3	28
9	3	3	1	31

Table 9
ANOVA table of the factors and their effects of the optimization experiments

	DF	Seq SS	Variance	*F*-ratio	Pure sum	Percent
Solvent composition (dimensionless)	2	20.222	10.111	22.746	19.333	16.4445
Solvent ratio (dimensionless)	2	88.222	44.111	99.235	87.333	74.29
Cooling rate (°C/min)	2	8.222	4.111	9.248	7.333	6.238
Residual error	2	0.888	0.444			3.027
Total	2	117.55				100.00 %

4. Conclusions

This study provides experimental data for the dewaxing process of an Iranian heavy raffinate sample provided by Isfahan Sepahan oil refinery. All the experiments are conducted by adopting a design of experiment technique (DOE) with a target of reducing the oil content of the produced wax. The effects of five factors are quantitatively determined and the appropriate levels are proposed for reducing the oil content. The results show that the solvent ratio is the most important factor in minimizing the oil content of the wax and has the highest effect and percent of contribution. The data show that an increase in the amount of MEK or MTBE as anti-solvents results in higher oil contents. A slow cooling rate usually promotes the growth of crystals with a multilayer spiral type of morphology, which causes oil occlusions and thereby leading to more oil content. Although, crystallization temperature impacts on the pour point needed for the oil produced, it has a negligible effect on the oil content of the wax. The performance of the two pairs of the solvents used here is similar and the oil content of the wax has not statistically changed remarkably. Thus, choosing the solvents mainly depends on their availability and price.

Using new filtering equipment and crystallizers to enhance the quality of the wax and oil produced is suggested for future works. The pulsed mixed crystallizers and nanofiltration methods would be a great substitution for the traditional dewaxing technologies. Furthermore, using modifiers as an additive in solvent dewaxing could have a great effect on the yield of separation and low oil content.

Nomenclature

Adj MS	: Adjusted mean of squares
Adj SS	: Adjusted sum of squares
DF	: Degree of freedom
DOE	: Design of experiments
MEK	: Methyl ethyl ketone
MTBE	: Methyl tert-butyl ether
MIBK	: Methyl isobutyl ketone
Seq SS	: Sum of squares
S/N ratio	: Signal to noise ratio
wt.%	: Weight percent

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