SIMULATIVE PROGRAMMING OF A HYBRID WASHING OIL SEPARATION SCHEME FOR PURE CHEMICALS

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Abstract: Washing oil, one of the important distillation cut of coal tar, consists of a series of high value-added components which can form azetropic and eutectic system, making it impossible to separate certain components completely by normal distillation. In this work, a scheme coupling distillation with crystallization to deal with this cut for pure chemicals is simulatively investigated before an industrial design. By the aid of this research, a 25Kt/a pilot scale unit was successfully designed which is now running with α-methyl-naphthalene, β-methyl-naphthalene, fluorene, dibenzofuran and acenaphthylene in high purity as main products and naphthalene fraction, medium washing oil (dimethylnaphthalene) and heavy washing oil as by-products.

1 INTRODUCTION

Washing oil is the distillation cut of coal tar between 230~300ºC, which consists of many organic chemical materials, such as naphthalene, methyl-naphthalene, dimethyl naphthalene, fluorene, dibenzofuran, acenaphthylene etc (Wang, 2004).

Basically, there are two ways to produce these substances of high purity, synthesis and separation. The cost of the former is undoubtedly high, while the physical separating way from washing oil is simple and proved to be economical (Liang and Xue, 2008). Therefore, deep processing of this cut through physical separative method becomes practically significant (Song and Schobert, 1993).

On the other hand, washing oil was widely available in coal based coking industry which is usually applied in washing benzene from coal gas, making this cut missed the opportunities for further deep utilization for more value-added fine chemicals, with the residue still remaining the above mentioned bulk features, or becomes even better. The good news is that the concern to separation options has been given rise to with the increasing demanding for fine chemicals, which can be extensively used in pesticides, pharmaceuticals, dyes, synthetic materials (Yang and Duan, 2006; González and Gutierrez, 2008), as well as the increasing large-scale of coal tar plant to offer more and more resource of washing oil .

In the present work, a novel scheme coupling distillation with crystallization for comprehensively deep processing of washing oil is reported, and subsequently simulatively researched and programmed from the angle of industrial design, with the recommended scheme then manifested to be feasible through successfully running over 12 months of a 25Kt/a pilot scale unit. By the aid of this research, this unit was designed with α-methylnaphthalene, β-methylnaphthalene, fluorene, dibenzofuran, and acenaphthylene as main product, and the naphthalene, medium washing oil, and heavy washing oil as byproducts.

2 MODELLA SCHEDULE

2.1 Crude Washing Oil Feedstock

The components of washing oil are listed in Table 1, some of which with low content cannot be defined by instrument analyses. One possibility for this situation is to select substitutes for the undefined components in the simulation calculation process, through assigning corresponding selected substances of different normal boiling points in accordance with chromatograph peak sequence.

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Table1: Components of original materials (washing oil) and their characteristics.

No.	Name	Boiling Point (℃)	Molecular Weight kg/kmol	Mass Fraction (wt%)
1	Naphthalene	217.96	128.175	3.849
2	Quinoline	237.69	129.161	3.023
3	X-01	239.73	144.210	0.817
4	X-02	239.73	150.220	1.732
5	X-03	240.75	149.236	0.285
6	β-methylnaphthalene	241.05	142.202	21.153
7	α-methylnaphthalene	244.69	142.202	10.020
8	X-04	246.50	134.134	0.108
9	X-05	247.80	143.188	0.165
10	X-06	247.96	143.188	0.278
11	X-07	248.11	172.310	0.136
12	X-08	249.85	122.124	0.099
13	Biphenyl	255.00	154.211	4.589
14	X-09	258.05	170.211	1.497
15	2,6-dimethylnaphthalene	262.00	156.227	3.244
16	X-10	264.85	220.354	0.093
17	1,3-Dimethylnaphthalene/ 1,4-Dimethylnaphthalene	263.00	156.227	4.697
18	X-11	267.00	198.349	1.320
19	X-12	268.39	105.138	0.319
20	indole	253.00	117.15	1.396
21	Acenaphthylene	277.39	154.21	18.88
22	X-13	282.05	204.356	1.380
23	Dibenzofuran	284.71	168.195	9.491
24	X-14	284.85	152.15	0.336
25	X-15	286.00	196.29	0.337
26	X-16	293.15	183.252	0.508
27	X-17	293.85	166.177	0.277
28	Fluorene	297.29	166.222	7.624
29	X-18	300.78	143.188	0.341
30	X-19	306.09	143.188	0.972
31	X-20	336.85	192.26	0.443
32	X-21	346.00	179.221	0.594

As shown in Table 1, the boiling points of the components in the mixture are so close. This implies high challenges for distillation requiring high purities of the distillates. Besides, many binary azeotropics, e.g. indole-acenaphthylene, indole-dimethylnaphthalene, together with some eutectics which summarized in Table 2 are formed in washing oil, which further increase the difficulty for completely the separation of single component.

Table 2: The main eutectics of washing oil.

Eutectic	Melting Point (℃)
Naphthalene/β-methylnaphthalene	26
Naphthalene/α-methylnaphthalene	-34.6
Naphthalene/acenaphthylene	51
Naphthalene/fluorene	57
Naphthalene/indole	41.8
β-methylnaphthalene/α-methylnaphthalene	-41

2.2 Flowsheet Description for Current Deep Processing of Washing Oil

Currently, washing oil was only rough finished or selectively separated for several components in China. A number of processing technics have already been reported, such as narrow fractions separating method, azeotropic distillation, extractive distillation, and combination of distillation and washing (Wang, 2004). However, all of these methods have extremely complex process with limited product species. Reportedly, the most recommended method was from the Chemical Co., Nippon Steel Corporation in Japan (Zhang and Yan, 2002). Their processing flowsheet is shown in Figure 1.

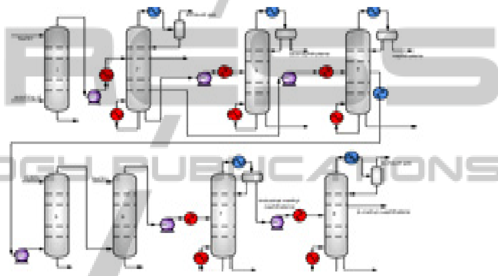

Figure 1: The washing oil processing flowsheet of The Chemical Co., Nippon Steel Corporation.
1- alkaline tower; 2-washed material distillation tower ; 3-acenaphthylene tower; 4-naphthalene tower; 5-acid tower; 6-neutralizing tower; 7-methyl naphthalene tower; 8-β-methylnaphthalene tower.

Washing oil is added to the alkaline tower after mixed with naphthalene oil, and NaOH solution is used as detergent to remove phenol. Then the washed material is heated and pumped to the distillation towers to separate low naphthalene oil, medium oil, and residual oil in sequence. Low naphthalene oil is used to recover benzene, residual oil to obtain industrial acenaphthylene in the next column, and medium oil is heated and then pumped to naphthalene tower to distill industrial naphthalene, methyl naphthalene, and residual oil. After that, the methyl naphthalene is pumped to the acid tower to remove pyridine and quinoline, and then neutralized using NaOH in neutralizing tower. Afterwards, industrial methyl naphthalene is obtained in methyl naphthalene tower, and further it also can be refined to β-methylnaphthalene. At the end, it can not only obtain β-methylnaphthalene of high purity, but also industrial naphthalene, industrial methyl naphthalene, industrial fluorene and medium washing oil.

This technic can not only use to separate washing oil, but also treat naphthalene oil and methylnaphthalene oil, with large capacity. In the process, methylnaphthalene oil was drawn in gas phase to avoid emulsification. As the five distillation columns are packed with high efficient packing, all the products are distilled to high purity, among which the purity of β-methylnaphthalene reached 98wt%. With all the packed columns operated in decompression, bottom temperatures are lowered and demands of heating medium of high temperature resisted. Besides, this process can take advantage of self-produced steam and warm water to reduce the energy consumption.

2.3 Novel Separation Process for Washing Oil

To make full use of the washing oil resource, a novel separation process was encouraged to present, as shown in Figure 2. Crude washing oil is first fed into naphthalene tower to obtain naphthalene cut. The residual oil is pumped into methyl naphthalene tower, where industrial methyl naphthalene can be recovered as top product which is then driven to the β-methylnaphthalene tower to produce β-methylnaphthalene and α-methylnaphthalene simultaneously. Moreover, the bottom α-methylnaphthalene stream can exchange heat with methylnaphthalene stream for sake of energy saving. Residual methylnaphthalene oil is pumped into acenaphthylene tower after mixed with crystalline raffinate from acenaphthylene crystallizer to distillate medium washing oil, crude acenaphthylene and residual acenaphthylene oil. And then the crude acenaphthylene is further refined by crystallization to obtain industrial acenaphthalene. Residual acenaphthalene oil is pumped into dibenzofuran tower for dibenzofuran with the bottom residual dibenzofuran oil driven into fluorene tower after mixed with fluorene crystallizer raffinate. The side product pumped to crystallization unit for industrial fluorene.

In the original flowsheet, fluorene is reclaimed from the top of T6, after crystallization, fluorene of industrial grade is obtained, and the residual liquid with a series of light components returns to the feed stream of T6. Consequently, the light components accumulated in the reflux and increased continuously, resulting in decrease of fluorene quality. As an improved process, the fluorene fraction is drawn out as a side-product, the light components is removed from the top of the column. This is just the starting point of the coupled scheme between ordinary distillation and crystallization. So in this scheme, α-methyl-naphthalene, β-methyl-naphthalene, fluorene, dibenzofuran, and acenaphthylene are simultaneously obtained in high purity, and the naphthalene fraction, medium washing oil (dimethyl naphthalene), and heavy washing oil can also be attained as by-product.

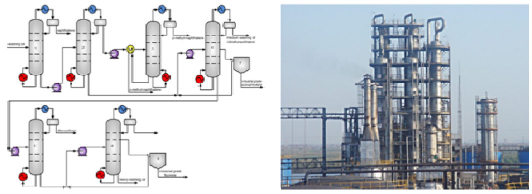

Figure 2: Flowsheet of distillation coupled with crystallization and its on-site counterparts
T1-naphthalene tower; T2-methylnaphthalene tower; T3-β-methylnaphthalene tower; T4- acenaphthylene tower; T5- dibenzofuran tower; T6-fluorene tower; 7-acenaphthylene crystallizer; 8-fluorene crystallizer

2.4 Simulative Design of Distillation Coupled with Crystallization Process

This novel process was simulatively analyzed with SRK-modified Panag-Reid equation of state (SRKM) and Grayson-Streed generalized correlations (GS), which were empirically confirmed by the co-authors in similar industrial practices to describe the basic thermodynamic behavior of the system appropriately. SRKM equation is an improvement for SRK equation to provide better predictions of properties for multicomponent systems:

$$\alpha_{ij} = (\alpha_i \alpha_j)^{1/2} \left\{ (1 \quad k_{ij}) + (k_{ij} \quad k_{ji})(x_i / (x_i + x_j))^{c_{ij}} \right\} \tag{1}$$

And GS correlation is a modification of the Chao-Seader correlation, which can be expressed as:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i}{\varphi_i}\left(\frac{f_i^{OL}}{P}\right) \tag{2}$$

$$\ln\left(\frac{f_i^{OL}}{P}\right) = \ln\left(\frac{f_i^{OL}}{P}\right)_0 + w\ln\left(\frac{f_i^{OL}}{P}\right)_1 \tag{3}$$

Besides, the purity of acenaphthylene and fluorene separated by crystallization was both set to be 97%, and their yield were 75% and 60% respectively according to the designers of the crystallizers. So in the process simulation, the above parameters are specified in the input procedures and the quantity of circumfluence from the crystallizers is calculated automatically.

In order to obtain simulative parameters that agree as well as possible with the on-site counterparts, hydraulic calculations of packings, and the pressure drops of the distributers are taken into account. That is, process simulation and structure design rise alternately, with the results of process calculation guiding the structure parameter design and structure design, in return, amending the process simulation. The operating parameters and the results of process simulation are listed in Table 3 and 4.

Table 3: The operating data of six columns in simulation.

	T1		T2		T3	
	Top	Bottom	Top	Bottom	Top	Bottom
N_T	100		100		120	
R	28		9		22	
Mr	134	152	141	159		
T(℃)	85	266	85	280	110	251
P (kpa)	105	114	105	114	80	115
	T4		T5		T6	
	Top	Bottom	Top	Bottom	Top	Bottom
N_T	100		100		104	
R	18		30		19	
Mr	158	166	168	164	169	154
T (℃)	85	295	85	304	85	320
P (kpa)	105	114	105	114	105	114

As shown, the purity of methylnaphthalene, β-methylnaphthalene, fluorene, and acenaphthylene all reach industrial grade. And actually the field date of this 25Kt/a pilot scale unit indicated that the purity of the 5 main products all go beyond 95wt%, which fully accommodated the requirements of fine chemicals.

Table 4: The components of main production in simulation.

No.	Methylnaphthalene	Acenaphthylene	Fluorene	β-methylnaphthalene
1	6.28E-10	0.0000	0.0000	9.25E-10
2	5.95E-03	9.15E-11	0.0000	8.7E-03
3	1.76E-04	3.14E-13	0.0000	2.59E-04
4	9.67E-03	1.57E-09	0.0000	0.0142
5	1.64E-03	3.52E-10	0.0000	2.42E-03
6	0.637	9.16E-07	0.0000	0.9201
7	0.306	8.18E-06	0.0000	0.0417
8	3.18E-03	1.26E-11	0.000	9.22E-05
9	2.64E-03	6.34E-06	0.0000	3.70E-03
10	5.71E-03	7.16E-06	0.0000	8.18E-03
11	7.77E-09	1.81E-17	0.0000	1.15E-08
12	2.95E-03	3.47E-12	0.0000	5.85E-04
13	3.31E-07	7.33E-04	0.0000	1.00E-16
14	1.27E-09	3.35E-04	0.0000	0.0000
15	4.89E-08	1.16E-03	0.0000	0.0000
16	9.24E-10	1.96E-03	0.0000	0.0000
17	7.21E-07	9.27E-13	0.0000	3.23E-16
18	3.29E-05	4.66E-04	0.0000	6.43E-20
19	0.0000	5.51E-05	0.0000	0.0000
20	0.0260	7.33E-11	0.0000	9.41E-08
21	0.0000	0.9695	4.07E-12	0.0000
22	9.75E-15	0.0182	0.0000	0.0000
23	1.46E-20	1.58E-03	1.68E-07	0.0000
24	2.02E-20	5.71E-03	1.36E-08	0.0000
25	0.0000	3.05E-05	0.0000	0.0000
26	0.0000	9.03E-08	1.15E-03	0.0000
27	0.0000	8.72E-09	1.47E-04	0.0000
28	0.0000	1.22E-04	0.9706	0.0000
29	0.0000	5.23E-06	0.0278	0.0000
30	0.0000	1.19E-07	2.77E-04	0.0000
31	0.0000	4.54E-05	1.44E-18	0.0000
32	0.0000	0.0000	2.44E-20	0.0000

3 CONCLUSIONS

A novel process based on distillation coupled with crystallization for the separation washing oil to reclaim high grade fine chemicals is presented in this work, from first step simulative research to the successful field fulfillment. It demonstrates that this process can utilize washing oil more comprehensively with up to 5 fine chemicals, namely, α-methyl-naphthalene, β-methyl-naphthalene, fluorene, dibenzofuran and acenaphthylene as principal products, and naphthalene fraction, medium washing oil (dimethyl naphthalene), as well as heavy washing oil of improved quality as byproducts. In addition, results from a converged simulation revealed these main products were in high purity, suggesting the feasibility of this hybrid scheme, which was then verified by field running data.

On this foundation, by the aid of high efficient packing technology, a 25Kt/a pilot scale unit was designed, and has already successfully run over 12 months.

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