

The Purification of Coal Tar by the Addition of Quinoline and $Zn(OH)_2$

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Summary: The coal tar was purified by the addition of quinoline and $Zn(OH)_2$, in order to decrease the content of carbon and inorganic oxide particles. The effect on the viscosity and ash content of the coal tar were investigated by altering temperature, time, and the amount of quinoline and $Zn(OH)_2$. When the volume ratio between quinoline and coal tar was 20:1 and the static time was 24 h. The viscosity of three layers decreased with rising temperature. When the static temperature and time was 45 °C and 24 h, respectively. The viscosity of three layers decreased with the arising amount of quinoline. And when the volume ratio between quinoline and coal tar was 20:1 and the temperature was 45 °C. The viscosity of three layers decreased first and then increased with the prolonging of static time. And when the static time of coal tar was 24 h, the viscosity of coal tar is the lowest. Because of the lower viscosity of coal tar, decreasing the content of carbon and ash particles in upper and middle layer, the ash content decreased from 0.168% to 0.092%. The addition of $Zn(OH)_2$ can lead ash content in middle layer decrease to 0.058%. Zn_2SiO_4 and $ZnAl_2O_4$ may be produced due to the reaction between $Zn(OH)_2$ and SiO_2 or Al_2O_3 , which can settle down easily. The results show that the content of carbon and inorganic oxide particles in upper-middle-class (the middle 4/5 of the whole volume) decreased with the addition of quinoline and $Zn(OH)_2$. When the volume ratio between quinoline and coal tar was 50:2, quality ratio between coal tar and $Zn(OH)_2$ was 20000:1, the mixture were heated up to 45 °C at atmospheric pressure and keeping this constant temperature for 24 h, the ash content in upper-middle-class can decreased to 0.058%.

Key words: Coal tar; Purification; Ash; Viscosity; Inorganic oxide particles

Introduction

Coal tar is a by-product from the pyrolysis of coal to produce coke for the steel industry, and widely used as raw materials in organic chemical [1, 2]. It is a complex mixture, consisting of a variety of compounds, in which only about 500 compounds have been identified, containing 174 kinds of neutral components, 63 kinds of acidic components and 113 kinds of alkali components. It is the main resource of polycyclic compounds and homologous heterocyclic compounds containing oxygen, nitrogen and sulfur. From 1822 to 1950s, the coal tar is the only raw material for the aromatic hydrocarbon chemistry, preservative oil, road asphalt, briquette binder *et al* [3-9].

Some tiny carbon particles and inorganic substances enter into coal tar because of mass transfer process such as gas flow and adhesion in the process of coal carbonization. Impurities in coal tar hinder industrial application of it [10-12]. The purity of the coal tar is the necessary step for utilizing these valuable resources efficiently. And Coal tar is a by-product from the pyrolysis of coal, so the purity of the coal tar is more important for the limited fossil fuel. There are some methods of purifying coal tar such as: distillation method, hot-filtering method, centrifugal sedimentation method, solvent extraction

method, and static settling method [13-16].

Distillation method is mainly used to remove the moisture in the coal tar and to separate the volatile components and pitches. It can be divided into atmospheric distillation, decompression distillation, and atmospheric-decompression distillation according to the operating pressure. This method is the general purification method of processing industry [17]. The distillation method has a low recovery rate from the study of decompression distillation. The content of QI decreased to 0.28% after decompression distillation [10]. The basic principle of hot-filtering method is that forcing the liquid-solid two-phase mixture get through porous media by the pressure. Solid particles would be intercepted on the medium, so as to achieve the purpose of the separation of coal tar and solid particles. The content of QI reduced to 0.36% after hot-filtering requiring micron aperture to separate impurity [10]. Centrifugal sedimentation method can separate the impurity out of coal tar on the basis of the action of centrifugal force. The accumulation of impurity will be more and more obvious as the centrifugal time prolonging and the rotational speed increasing. Therefore, centrifugal sedimentation method can be used as a physical method of

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purification of coal tar. Centrifugal sedimentation method can make ash content reduce to 0.1%, and can't be industrialized. The other physical way to reduce the impurity in coal tar is adding solvent. Coal tar is mixture of various organics, the purification of coal tar can achieved by adding organic solvents as extraction agent on the basis of similar dissolve mutually theory. This method can purify light constituent from coal tar distilled oils [18, 19]. Solvent extraction method can only separate volatile similar mixed liquid, and needs a lot of organic solvents [14]. Static sedimentation separation is a simple method to purify coal tar, which is easy to operate. But it is hard to master the best temperature and static time. Ash content only reduced to 0.25% using sample static sedimentation separation [15].

Most of the above studies can not reduce the amount of ash efficiently. The addition of quinoline and $Zn(OH)_2$ can purify coal tar and decrease the content of carbon and inorganic oxide particles. Altering temperature, time, the amount of quinolone and $Zn(OH)_2$ can effect the viscosity and ash content of the coal tar. Viscosity of the coal tar can be controlled by altering treatment conditions. The decrease of viscosity can make the larger solid particles settle down. The reaction between $Zn(OH)_2$ and SiO_2 or Al_2O_3 can make the solid particles become bigger, which lead to particles settle down easily. Thus, the content of carbon and inorganic oxide particles such as SiO_2 and Al_2O_3 coal tar decreased by the treatment of quinolone and $Zn(OH)_2$. This purifying method lays a foundation for further use of pitches.

Experimental

Materials

The coal tar sample studied in this work was collected from a Coking Plant in Guizhou province. Quinoline, analytically pure, Shanghai mountain pu chemical engineering LTD; ammonium hydroxide, analytically pure, Chengdu jinshan chemical reagent LTD; zinc hydroxide, Tianjin yongda chemical LTD.

Method

Solid particles were obtained by using quinoline repeatedly washing coal tar until it became clear solution. The static sedimentation method was employed to purify coal tar stirring evenly after mixed with suitable amount of quinoline and $Zn(OH)_2$.

Determination and Characterization

The viscosity of coal tar was measured by Engler viscometer (WNE-1A, yutong instrument industry, Shanghai, China). Ash content of coal tar was tested according to GB/T 2295-2008. The chemical composition of the solid particles was tested according to GB/T 1574-2007. The size distribution of solid particles was determined by laser particle size distribution instrument (BT-9300H, baite instrument industry, dandong, China). Micro-morphology was measured by SEM (ZEISS, ZEISS, Germany).

Results and Discussion

The Effect of Static Conditions on the Viscosity and Ash Content of Coal Tar

Temperature

Volume ratio between quinolone and coal tar was 20:1 and the static time was 24 h. The influence of temperature on the viscosity of coal tar was listed in Table-1.

Table-1: The influence of temperature on the viscosity of coal tar.

Temperature/°C	Viscosity/mpa·s		
	Upper layer	Middle laye	Under layer
35	704.5	736.5	750.0
45	344.9	354.8	358.1
55	113.5	122.6	128.7

Table-1 lists the viscosity of three layers decreased with rising temperature. The reason is that molecules activity heightened and forces among molecules decreased with the temperature increasing. The viscosity spread between the three layers was caused by the molecular weight difference. The viscosity of under-layer coal tar is the largest resulting highest viscosity. Molecular motion is more intense as the temperature increasing, that is why the viscosity spread decreased.

The influence of temperature on ash content in coal tar (middle layer) was displayed in Fig. 1

Fig. 1 shows that ash content decreased from 0.116% to 0.102% with rising temperature, and then ash content increased along with temperature exceeds 45 °C. Table-1 lists that viscosity decreased with rising temperature. The decreasing of viscosity should be conducive to the settlement of solid particles, but at the same time solid particles doing

Brownian motion. The diffusion coefficient of coal tar particles:

$$D = kT / 6\pi\mu d \quad (1)$$

where

k —Boltzmann constant, T —temperature, μ —viscosity of fluid power, d —particle diameter.

D increased with temperature increasing, and then Brownian motion of particles increased. The Brownian motion exceed the gravity sedimentation of particles causing particles constant movement in coal tar, which results in ash content increased.

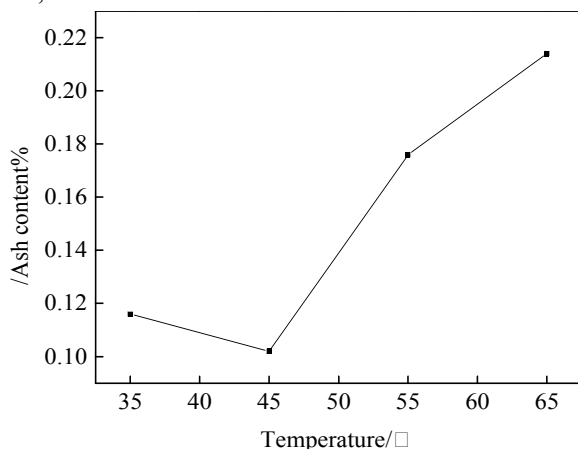


Fig. 1: The influence of temperature on ash content in coal tar.

The Amount of Quinoline

The static temperature and time was 45 °C and 24 h, respectively. The influence of the amount of quinoline on the viscosity of coal tar was listed in Table-2.

Table-2 lists the viscosity of three layers decreased with the rising of the amount of quinoline. Forces among molecules decreased with the addition of quinoline, because of quinoline has strong solubility and bond broken function. Meanwhile, the molecular weight difference decreased with the rising of the amount of quinoline that is reason that the viscosity spread decreased.

Table-2: The influence of the amount of quinoline on the viscosity of coal tar.

$V_{\text{coal tar}}:V_{\text{Quinoline}}$	Viscosity/mpa·s		
	Upper layer	Middle laye	Under layer
100:3	455.0	469.3	488.5
50:2	384.0	400.2	416.0
20:1	344.9	354.8	358.1

The influence of the amount of quinoline on ash content in coal tar (middle layer) was displayed in Fig. 2.

Fig. 2 shows that ash content decreased from 0.168% to 0.092% with the rising of the amount of quinoline, and then ash content increased with volume ratio between quinolone and coal tar greater than 50:2. Table-2 lists that viscosity of upper layer is lowest, middle and under layer's viscosity is similar as the volume ratio between quinolone and coal tar was 20:1. Therefore, the solid particles in upper layer were settle down easily, but in middle layer were hard to settle down due to the viscosity. That is why ash content increased.

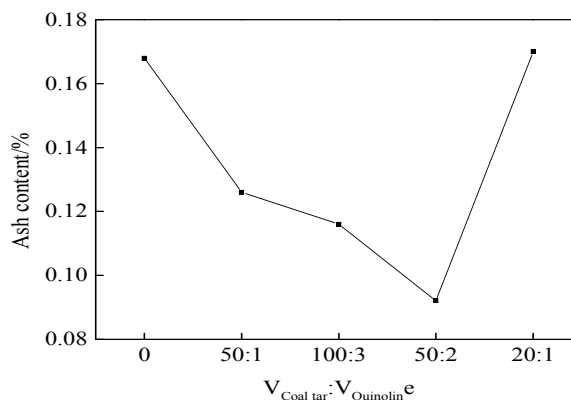


Fig. 2: The influence of quinoline addition on ash content in coal tar.

Static Time

The influence of static time on the viscosity of coal tar was listed in Table-3, on the condition that the volume ratio between quinolone and coal tar was 20:1 and the temperature was 45 °C.

Table-3: The influence of time on the viscosity of coal tar.

time/h	Viscosity/mpa·s					
	(a)			(b)		
	Upper layer	Middle layer	Under layer	Upper layer	Middle layer	Under layer
20	465.2	479.8	497.5	465.2	479.8	497.5
24	344.9	354.8	358.1	344.9	354.8	358.1
28	487.7	508.5	530.3	387.7	398.5	410.3

Table-2 displays under the circumstances the viscosity of coal tar was the lowest and forces among molecules decreased. But Table-3 lists the viscosity of three layers in (a) experiment decreased

first and then increased with the prolonging of static time. Two reasons may lead to the increase of viscosity: the volatilization of small molecules; the reaction between molecules. Beaker was filled up with coal tar and covered with plastic wrap in (b) experiment. The viscosity also increased after 28 h static sedimentation. Hence, the main reason that results in the increase of viscosity was the reaction between molecules. Therefore, the static time of coal tar should not be more than 24 h.

The temperature was 45 °C and volume ratio between quinolone and coal tar was 50:2 (as shown in Fig. 2). The influence of static time on ash content in coal tar (middle layer) was displayed in Fig. 3.

Fig. 3 shows that ash content decreased with the prolonging of static time. No further increase in the ash content as static time longer than 24 h. Table-3 lists that viscosity increased with static time longer than 24 h, which leads to solid particles hard to settle down. That is the reason why ash content stops increasing.

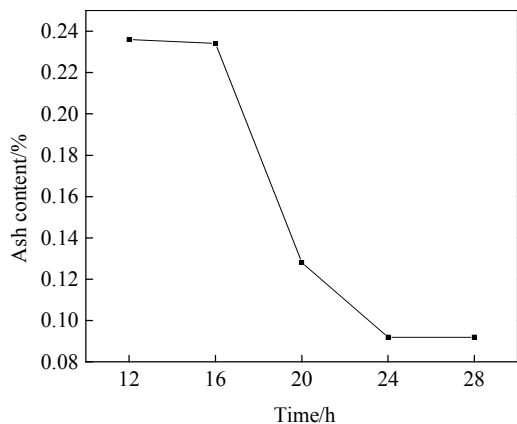


Fig. 3: The influence of time on ash content in coal tar.

The Effect of the Amount of Zinc Hydroxide on Ash Content of Coal Tar

Volume ratio between quinolone and coal tar was 50:2, the temperature was 45 °C, and the static time was 24 h. The effect of the amount of zinc hydroxide on ash content of coal tar was shown in Fig. 4.

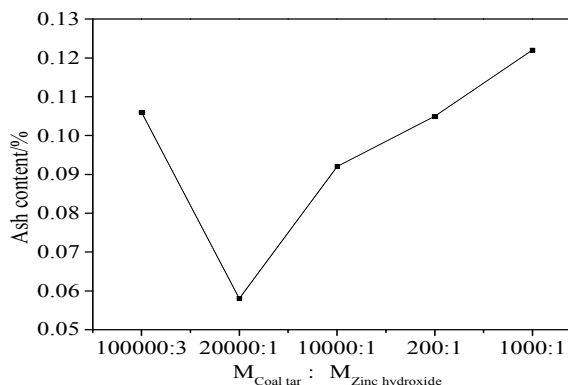


Fig. 4: The influence of zinc hydroxide on ash content in coal tar.

Fig. 4 shows ash content decreased first and then increased with the rising of quality ratio between coal tar and Zn(OH)₂. Ash content can reach 0.058% on the condition that quality ratio between coal tar and Zn(OH)₂ was 20000:1. Reduction of the content of SiO₂ and Al₂O₃ in ash can be achieved by the addition of Zn(OH)₂, while, Zn(OH)₂ turned into ash as Zn(OH)₂ excessive.

Physical Property and Micro-Morphology Analysis

Particle Size Analysis

Solid particles were taken from the coal tar that diluted by quinolone at the ratio of 50:2 then heated up to 45 °C and keeping this constant temperature for 24 h. Solid particle size distribution of various layers was listed in Table-4.

Table-4: The particle size distribution of solid particles in each layer.

Particle size/ μm	Upper layer	Middle layer	Under layer
0.000-2.000	23.35%	23.65%	21.67%
2.000-20.00	74.35%	73.56%	74.56%
20.00-200.0	2.30%	2.79%	3.77%

The distribution of particle size was from 0 to 200 μm . The proportion of 2-20 μm is the largest, while, proportion of 20-200 μm is the minimum and under layer has the largest proportion of 20-200 μm .

Table-1 shows that viscosity is the lowest at 55 °C, the obstruction that hinders particles to settle down decreased. At the same time solid particles doing Brownian motion. The diffusion coefficient of coal tar particles:

$$D=kT/6\pi\mu d \quad (1)$$

Brownian motion becomes fiercer as d decreased. The Brownian motion exceeds the gravity sedimentation of particles, causing particles constant movement in coal tar. That is why middle and under layers contains 0-20 μm particles. Similarly, upper layer also include 20-200 μm particles.

Measurement of Chemical Component

The ingredient content of ash in various layers listed in Table-5.

Table-5: The ingredient content of ash in every layer coal tar.

Ingredient	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	CaO	
Before treatment	Upper layer	15.08%	44.64%	26.73%	2.27%	0.20%
	Middle layer	16.82%	44.22%	24.30%	2.64%	0.60%
	Under layer	22.54%	43.38%	20.39%	3.45%	0.30%
After treatment	Upper layer	31.15%	24.38%	19.46%	10.38%	3.05%
	Middle layer	30.05%	23.20%	18.47%	10.40%	4.50%
	Under layer	21.18%	40.85%	23.47%	3.75%	0.70%

Table-5 displays that the most abundant composition is SiO₂, Al₂O₃ and Fe₂O₃ in various layers. After the treatment of Zn(OH)₂, the reaction between SiO₂ and Zn(OH)₂ may produced silicate and reaction between Al₂O₃ and Zn(OH)₂ may generated aluminate, which lead to the content of SiO₂ and Al₂O₃ decreased. The formation of silicate and aluminate results in solid particles grew up and settles down easily. So, under layer still contains high content of SiO₂ and Al₂O₃.

The content of carbon and ash particles in coal tar treated by different conditions was listed in Table-6.

Table-6: Content of solid particles.

		Solid particles containing /%	The content of carbon particles /%	Ash content /%
55 °C, 6mL, 24h	Upper layer	0.108	0.104	0.004
	Middle layer	0.104	0.098	0.006
	Under layer	0.108	0.076	0.032
45 °C, 10mL, 24h	Upper layer	0.212	0.204	0.008
	Middle layer	0.134	0.124	0.008
	Under layer	0.166	0.140	0.026
55 °C, 8mL, 28h	Upper layer	0.228	0.220	0.008
	Middle layer	0.088	0.072	0.016
	Under layer	0.152	0.074	0.078

Some particles unable to filter out from quinolone, so the content of solid particles were lower. Table-6 shows that the content of solid particles was lowest in middle layer. Upper layer has high content of carbon particles and under layer possesses high content of ash.

SEM Analysis

The SEM figures of solid particles before and after Zn(OH)₂ treatment were displayed in Fig. 5.

Fig. 5 shows that solid particles have two kinds of micro-morphology: sphere and acicular. Acicular particles possess smaller superficial area, therefore, acicular particles settle down easily than sphere particles as they possess similar quality. Thus, the under layer has more acicular particles. After the treatment of Zn(OH)₂ solid particles grew up and settle down more easily, while, the upper and middle layer has little acicular particles.

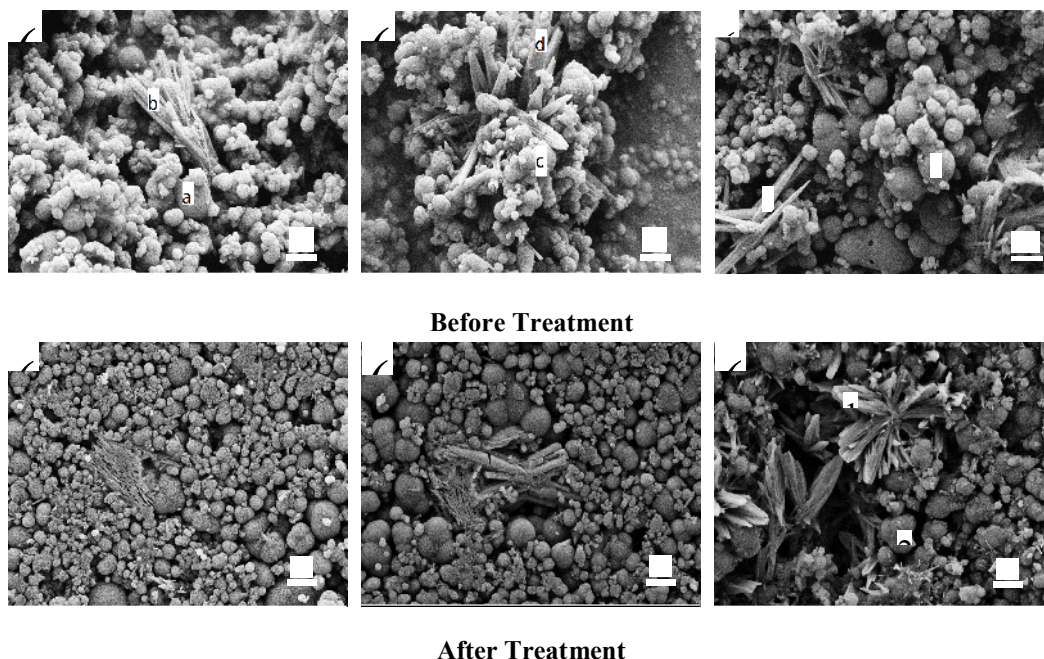
The weight percentage of different element of the standing of 1, 2 in Fig. 5 were listed in Table-7.

Table-7: The weight percentage of each element in the lower layer after treatment.

	C	O	Na	Cl	S	Al	Si	Fe	Zn
1	17.48	36.52	20.97	0.77	2.61	4.58	0.02	0.77	16.29
2	41.91	22.40	19.02	1.06	3.51	1.34	0.23	1.12	9.40

Table-7 shows that weight percentage of Al in standing 1 is higher than standing 2, which may be due to the formation of ZnAl₂O₄. Whereas weight percentage of Si in standing 2 is higher than standing 1, which may be due to the formation of Zn₂SiO₄. That is the reason that solid particles grew up and settle down more easily. There are little amount of ash in coal tar, and the addition of Zn(OH)₂ can not decrease all of ash. So, we currently unable to detect the presence of ZnAl₂O₄ and Zn₂SiO₄. But from the energy spectrum we can see there are Si, Al, Zn and O, and according to acid and alkaline of metal compounds we speculate the presence of ZnAl₂O₄ and Zn₂SiO₄.

The weight percentage of different element in the standing of a-f in Fig. 5 was listed in Table-8.



(a) upper layer, (b) middle layer, (c) under layer

Fig. 5 The scanning electron micrographs of solid particles in the every layer coal tar

Table-8: The weight percentage of each element in different shapes solid particles.

	C	O	Na	Cl	S	Al	Si	Fe
a	94.02	5.78	0.2					
b	66.37	28.52	5.00	0.10				
c	84.07	13.83	2.11					
d	46.14	39.57	13.17	0.19	0.69			0.23
e	95.73	4.04			0.23			
f	51.45	39.83	8.00	0.07		0.24	0.40	

Table-8 shows that sphere particles have higher carbon content, while possess little other elements. Some oxygen-containing heterocyclic compound dehydrogenized with abundant of aromatic compounds in the pyrogenation process of coal. Thus, sphere particles have higher carbon content and little oxygen content. Containing minute quantity of Na, S, etc. may be because the inorganic Na_2O , SO_3 in coal were wrapped in the process of pyrogenation. Whereas acicular particles possess lower carbon content, higher oxygen content and metallic element such as Al, Fe. Mesophase compounds were derived from the polymerization/condensation between aromatic hydrocarbon and phenols, heterocyclic compound in the pyrogenation process of coal. Mesophase sphere grow up or to coalesce with each other constantly. The regularly ordering of mesophase compounds along the direction of airflow was promoted by the flow of the gases [20], which lead to the formation of acicular

particles. Meanwhile, some metallic element in inorganic can activate aromatic hydrocarbon then accelerate the production and coalescence of mesophase sphere [21]. That interprets the reason that acicular particles possess some metallic element.

Conclusions

1. The viscosity of coal tar can be controlled by altering the temperature, the amount of quinoline and static time. Consequently, decreasing the content of carbon and ash particles in upper and middle layer, ash content decreased from 0.168% to 0.092%.
2. The addition of $\text{Zn}(\text{OH})_2$ can lead ash content in middle layer decrease to 0.058%. SiO_2 and Al_2O_3 may react with $\text{Zn}(\text{OH})_2$ and then generate components which easily settle down such as Zn_2SiO_4 and ZnAl_2O_4 .
3. The excellent purification condition: the volume ratio between quinolone and coal tar was 50:2, quality ratio between coal tar and $\text{Zn}(\text{OH})_2$ was 20000:1, the mixture were heated up to 45 °C at atmospheric pressure and keeping this constant temperature for 24 h, then ash content in upper-middle-class can decreased to 0.058%.

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