Pak J Sci Ind Res 2003 ***46*** *(2) 78-80*

ACIDITY OF THE EEFLUENTS PRODUCED DURING AIR BLOWING OF ASPHALT

M A Quddus**[*a], S N Sarwar [a] and F Khan [b]

[a]*Hydrocarbon Development Institute of Pakistan, Karachi 75400, Pakistan*

[b]*Department of Applied Chemistry, University of Karachi 75270, Pakistan*

(Received 19 January 2002; accepted 16 April 2002)

The effluents (distillate) obtained during air blowing of asphalt in presence of metallic salts, were evaluated for their amount, gravity and acidic content. The acidic gases decrease the life of the plant and cause environmental problems. During a 15 h air oxidation (blowing) period, it was observed that for feed-I, amount and acidity were effected by the catalysts. Variation in the amount and gravity of effluents during feed II and III air blowing was not so distinct as with feed I. This indicates that the extent of amount and acidic content of the effluents also depend on the composition of feed.

Key words: Asphalt, Air blowing, Catalyst, Acidity, Effluent.

Introduction

Air blowing of petroleum asphalt is carried out to increase the hardening and temperature susceptibility of the end product (Sheorn and Hoiberg 1953). This air blowing is carried out with or without catalyst (Corbet 1970). Invariably significant acidity is produced in the effluents along with low boiling point hydrocarbons, hydrogen sulfide, carbon dioxide, carbon monoxide and water vapours. These effluents, sometime called blowing losses may vary upto 10% depending upon the properties, consistency of the feed asphalt, operating conditions (temperature, air rate) and design of the plant. Many papers on air blowing of salts are Kuriakose and Manjooran (1994), Speight (1999). This paper studies the quality of effluents (distillate), produced by using three different feed asphalts with ten different catalysts, in terms of their gravity and acidity.

Experimental

A mild steel cylindrical reactor of height 60 cm and diameter 36 cm having provision for introduction of air near the base was utilized for air blowing of asphalt. The feed asphalt was taken in the reactor and the air blowing was carried out at the rate of 0.08 ft^3, min^{-1} kg^{-1} at 240°C for 15 h. The detail of the reactor and procedure for air blowing of feed asphalts (I, II and III) has been reported by Quddus and Khan (1990).

The effluent from the reactor first passed through an air-cooled condenser where most of the heavy oil was condensed and taken into a knockout vessel. The remaining gases then passed through a set of scrubbers containing distilled water. The uncondensed gases, which mostly contain air, were vented out. After each experiment, the contents of the knock out vessel and water scrubbers were mixed thoroughly and warmed to about 60°C and taken into a separatly funnel and kept overnight for the separation of water and oil layers. The appearance and quantity of oil was recorded. Specific gravity was determined by taking distillate oil sample in a cylinder, placed in a water bath for a given period of time, so that temperature equilibrium is attained. Using appropriate hydrometer, the specific gravity was recorded according to ASTM (1998). Extracted acidity in the water layer was determined, in term of milliequivalent per litre, by titrating with standard sodium hydroxide solution, using phenolphthalein as indicator.

Results and Discussion

The effect of various catalysts on the amount, specific gravity and acidity of effluents from feeds I, II and III is given in the Table 1. The chlorides of nickel, manganese and magnesium at 0.3% level produced almost the same amount of distillate having similar color (yellowish) as the blank test (without catalyst). In the same way these salts did not substantially accelerate the blowing reaction in decreasing the penetration or increasing the softening point of product asphalt (Quddus and Khan 1991). Using chlorides of stannic, chromium and cobalt, the amounts of effluents were comparable, as did the hardness of the product and the color of the effluents oils were darker as compared to the effluents from nickle, manganese and magnesium salts. Highest gravity together with highest amount of distillate was obtained using ferric chloride and the oil was still more darker (dark brown).

*Author for correspondence

At 0.6 wt.% catalyst concentrations, the amount, gravity and acidity of effluent showed an increasing trend. Catalyst like cobalt and zinc chlorides at 0.6 wt.% level were not very effective in reducing the time of blowing to reach at a given hardness. Similar behavior was also observed with respect to the amount and acidity of effluent i.e., cobalt and zinc did not respond to increasing catalyst concentration. The increased amount of copper, stannic and iron chlorides (0.6%) produced higher amount of heavier distillates alongwith sludge formation. The sludge was as high as 20% of the distillate when 0.6 wt.% ferric chloride was used. The color and appearance of the effluent oils produced by ferric and stannic chlorides were darker than the oils obtained using other catalysts. These oils have a tendency to form emulsion with water.

The mixed catalyst (0.3 wt.% metal chloride with equal amount of manganese dioxide) resulted in lesser amount of effluents for blown asphalt of almost similar hardness of blown product. The acidity and gravity had intermediate values as shown in the Table 1.

The response of feeds II and III were investigated at 0.3 wt.% on selected catalysts and the results are shown in the Table 1. Using same catalyst the amount of distillate increased especially with feed III. However, due to higher amount of distillate, less changes in color and specific gravity were noticed.

A comparison of results in Table 1 shows that higher amount of effluents were obtained, when feeds II and III were used (density 1.009 and 0.9965 and viscosity 533 and 1026 cSt. at 100°C respectively) as compared to feed I (density 1.0140 and viscosity 3797 cSt. at 100°C). This indicate that effluent is partially connected with lighter hydrocarbon constituents of the feed, which are distilled off at the blowing temperature (240°C). However a close observation of the physical data given in the Table 1 further indicates that under the same conditions of blowing, not only the amount of blown distillate were different but also their physical appearance and parameters studied, (specific gravity and acidity) were different for different catalysts.

Acidity as measured by titrating the water extract of the effluent oils was mainly, due to hydrochloric acid produced from

Table 1

Wt.%, Specific gravity and acidity of effluents

Catalyst		Feed I			Feed II			Feed III		
		Effluents Wt.%	Sp. Gravity 15.5/15.5°C	Acidity meq	Effluents Wt.%	Sp. Gravity 15.5/15.5°C	Acidity meq	Effluents Wt.%	Sp. Gravity 15.5/15.5°C	Acidity meq
Nil	-	2.0	0.9211	25	3.4	0.8467	58	7.0	0.8831	30
Nickel chloride	(0.3%)	2.4	0.9215	37	-	-	-	-	-	-
Manganese chloride	(0.3%)	2.5	0.9209	38	-	-	-	-	-	-
Stannic chloride	(0.3%)	2.7	0.9234	146	-	-	-	-	-	-
	(0.6%)	4.1	0.9322	253	-	-	-	-	-	-
	+(MnO_2)	3.8	0.9290	190	-	-	-	-	-	-
Chromium chloride	(0.3%)	2.6	0.9396	85	-	-	-	-	-	-
	(0.6%)	2.9	0.9559	205	-	-	-	-	-	-
	+(MnO_2)	2.8	0.9435	105	-	-	-	-	-	-
Zinc chloride	(0.3%)	2.4	0.9208	57	3.9	0.8762	90	8.4	0.8920	80
	(0.6%)	2.8	0.9501	83	-	-	-	-	-	-
	+(MnO_2)	2.7	0.9447	60	-	-	-	-	-	-
Cobalt chloride	(0.3%)	2.5	0.9388	59	3.5	0.8565	85	8.5	0.8989	74
	(0.6%)	2.6	0.9483	110	-	-	-	-	-	-
	+(MnO_2)	2.7	0.9450	84	-	-	-	-	-	-
Copper chloride	((0.3%)	3.0	0.9317	72	4.0	0.8805	122	8.3	0.8906	95
	(0.6%)	3.9	0.9552	108	-	-	-	-	-	-
	+(MnO_2)	3.0	0.9431	83	-	-	-	-	-	-
Ferric chloride	(0.3%)	2.7	0.9280	82	4.0	0.8820	310	9.3	0.8991	216
	(0.6%)	5.1	0.9606	205	-	-	-	-	-	-
	+(MnO_2)	3.3	0.9407	160	-	-	-	-	-	-
Magnesium chloride	(0.3%)	2.1	0.9235	39	-	-	-	-	-	-
Magnesium dioxide	(0.3%)	2.0	0.9277	27	-	-	-	-	-	-

decomposition of metal chloride catalyst. Blank test (without catalyst) also indicated some acidity and this is due to chlorine, carbon and sulfur compounds produced during air blowing reactions (Kirk Othmer 1978). Table 1 shows that maximum acidity was obtained for stannic, chromium and ferric chlorides when used in 0.6wt% concentration. All these salts are not very stable under the prevailing conditions of temperature (240°C) in the reactor and in presence of oxygen (air), and water vapours produced during air blowing. Stannic chloride is low melting point salt and rapidly under go hydrolysis to form hydrochloric acid and oxide. Copper, zinc, and cobalt chlorides are comparatively stable at the blowing conditions, their acidity are close to each other and much less than produced by ferric, chromium and stannic chlorides. Least active catalysts i.e., chloride of manganese, nickel and magnesium produced acidity which was comparable with blank test. The acidity of effluents using mixed catalyst was higher than 0.3% chloride catalyst but much lower than 0.6% chloride catalyst.

Ferric chloride could be termed as the best catalyst as far as hardening of asphalt is concerned. However, the effluent produced is maximum when ferric chloride is used as catalyst. The sludge formation of the effluent oil, which has increased to 20% of the total distillate further restrict its use as a catalyst. In absence of sludge and less acidity the effluents could be used as fuel oil and their disposal would pose no problem. Due to higher acidity of effluents the plant life would be greatly reduced or the initial cost of the plant would increase because of expensive corrosion resistant material of construction.

As an alternate the mixed catalyst ($FeCl_3$ + MnO_2) may be considered. It furnishes a product, which is reasonably good from end point usage; at the same time sludge formation and effluent produced are less and of relatively low acidity.

Conclusion

The study on effluents leads to the following conclusion. The amount and the acidity of the effluents are related to both the nature of feed and catalyst.

Active catalysts usually produce non-reusable emulsion forming effluent oil. The amount of effluent could be reduced and usefulness increases by use of mixed catalyst.

On the basis of acidity, one set of catalysts comprising stannic, chromium and ferric chlorides are highly active. Another set of catalysts comprising manganese, nickel, magnesium chlorides are least active, where as copper, zinc and cobalt chlorides have intermediate value.

References

ASTM 1998 *Annual Book of ASTM Standard on Gravity, Specific Gravity of Petroleum Products by Hydrometer Method,* D-1298.

Corbet L W 1970 Reaction variables in the air blowing of asphalt. *Ind Eng Chem Process Des Dev* **14**(2) 181.

Kirk Othmer 1978 *Encyclopedia of Chemical Technology*. Wiley Interscience Publication New York **3** pp 299.

Kuriokase, Manjooran 1994 Utilization of refinary sludge for lighter oil and industrial asphalt. *Energy Fuels* **8** (3) 788-92.

Quddus M A, Khan F 1990 Factors influencing asphalt oxidation. *Fuel* **69** 509.

Quddus M A, Khan F 1991 Catalytic air blowing of asphalt. *Chem Eng Tech VCH* **63**(2) 170.

Shearon W H, Hoiberg A J 1953 Catalytic asphalt. *Ind Eng Chem* **45** 2122.

Speight J G 1999 *The Chemistry and Technology of Petroleum*. Marcel Dekker Publisher N Y, USA.