RESEARCH ARTICLE OPEN ACCESS

To Study the Effect of Temperature on Pyrolysis of Crude Oil Washing Waste

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ABSTRACT
Crude Oil Washing (COW) waste is an emulsion of sediments mainly bottom hydrocarbon with water. It is unavoided product form during transportation and storage of crude oil when cargo tanks have been emptied or storage vessels are washed out. Exposure to COW waste causing health problems to eyes, skin and respiratory system. COW waste is black in colour and difficult to process as it is in an emulsion form. A research work has been carried out to study the effect of temperature on pyrolysis of COW waste. It shows that pyrolysis of COW waste at lower temperature gives more lighter product than the high temperature pyrolysis.
Keywords – Crude oil washing, Environment and COW Waste, Pyrolysis, Pyrolysis of COW waste.

Date of Submission: 16-11-2017 Date of acceptance: 28-11-2017

I. INTRODUCTION

Crude oil washing (COW) waste is washing out residue from the tanks of an oil tanker using the crude oil cargo itself, after that cargo tanks have been emptied. Crude oil washing (COW) is a system whereby oil tanks on a tanker are cleaned out between voyages (travel or passage) not with water, but with crude oil – the cargo itself. When oil cargo is sprayed with pressure on tank walls and surfaces, the sediments sticking to the tank dissolves and converts into useful cargo which can be pumped out to the shore tanks. This process is known as Crude Oil Washing.[1, 2, 3, 4, 5, 6, 7]

There are various methods of crude oil washing based upon technique used, these are:

1. Water washing,
2. Desalting,
3. Manual washing and
4. Crude Oil Tank OSWTE Technology.

The recent technology is crude oil tank OSWTE technology. This technology uses jetting washing machine to spray cleaning medium under a certain temperature, pressure and flow rate into the surface to be washed to remove the coagulation and sludge on it and to dispose and reclaim them later. The cleaning medium is crude oil. According to the work requirement and field condition, hot water and diesel oil is also used as cleaning medium after crude oil washing.

Exposure to crude oil washing waste causes health problems like:

a) Irritate the eyes, skin and respiratory system.

b) It may cause dizziness, rapid heart rate, headaches, confusion, and anemia.

c) Prolonged skin contact with crude oil washing waste may cause skin reddening, and burning of the skin.

When crude oil washing waste is burned, either accidentally, it emits chemicals that affect human health. These chemicals include carbon dioxide, carbon monoxide, lead, nitrogen oxides, particulate matter, polycyclic aromatic hydrocarbons, sulfur dioxide, and volatile organic compounds.[8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]

II. AIMS AND OBJECTIVES

Crude oil washing waste, 'COW' waste is black in colour, solid at room temperature, sticky in nature and very difficult to process. When heated it form the foam with trickling sound. To convert COW waste into useful product, literature survey was carried out, very less data is available for COW waste.[4, 5, 8, 13, 19, 20]

When COW waste is subjected to pyrolysis, it is observed that it gives lighter hydrocarbon product of fuel range. Thus it is an aim to study the effect of temperature on pyrolysis of COW waste to obtain fuel.

III. MATERIALS AND METHODS

To study the effect of temperature on pyrolysis of COW waste, initially after characterization of COW waste, it is de-emulsified followed by dehydration. Then this de-emulsified and dehydrated COW waste sample is used as feed for pyrolysis study. Following experimental techniques are adopted for pyrolysis study:

a) Characterization of dehydrated COW waste sample,

b) Pyrolysis of dehydrated COW waste (batch process) at three different possible temperatures,
c) Characterization of crack product obtained at three different temperatures,
d) Measurement of time-temperature data,
e) Material balance.

For pyrolysis study, instead of glass reactor specially designed stainless steel reactor with an arrangement of feed temperature measurements, product vapor temperature measurement, outlet for product is adopted.[21] To cool the product and to liquefied the product 3 stage condenser system is used.

As reactor capacity is of 2 liter volume, for safety a liter of COW waste that measured 840-860 gm is taken for batch of pyrolysis. The product is collected in a calibrated mark reservoir i.e. measuring cylinder. The time and temperature yield data during pyrolysis is also recorded. As to avoid wax deposition, product vapor cooling is done by using tap water (i.e. water at room temperature). Hence wax deposition in condenser line is negligible but little vapor losses observed at product collection point.

The crack product of each batch after pyrolysis is subjected to various testing as per IP/ASTM norms. The testing included the determination of following parameters.[2, 22, 23, 24, 25]

1. Density/specific gravity, API Gravity at 15.6^{0}C,
2. Viscosity at 40^{0}C (by using "U" tube viscometer),
3. Pour point,
4. Smoke point,
5. Aniline point,
6. Flash point (Cleveland Open Cup),
7. Conradson carbon residue (CCR),
8. Copper corrosion at 50^{0}C,
9. ASTM Distillation,
10. Acid value,
11. Saponification value,
12. Refractive index (20^{0}C),
13. Calorific value,
14. Moisture content (Karl-Fischer Auto-titrator).

IV. RESULTS AND DISCUSSION

As pyrolysis is nothing but dissociation of high molecular weight of hydrocarbon into lighter one.[2, 24, 25] As per literature survey cracking changes the properties as follows:

Characterization factor, boiling point, pour point, viscosity are decreases, unsaturation and aromatization increases, octane number increases, oxidation stability decreases.

Table 1: Comparison of properties of cracked liquid product at 425, 450 and 475^{0}C

S. N.	Properties	Feed (hydrated)	Feed (dehydrated)	Cracked product from 425^{0}C batch	Cracked product from 450^{0}C batch	Cracked product from 475^{0}C batch
1	Specific gravity	0.9431 at (80^{0}C/80^{0}C)	0.8609	0.808 (20^{0}C/20^{0}C)	0.8125 at (16^{0}C/16^{0}C)	0.8134 at (16^{0}C/16^{0}C)
2	API gravity, ^{0}API	18.5337	32.8628	43.62	42.6538	42.4611
4	Viscosity, cSt, at 40^{0}C	220 (75^{0}C) Redwood Sec. (by RW no. I)	151 (75^{0}C) Redwood Sec. (by RW no. I)	3.87	6.574	6.7865
5	Flash point, ^{0}C, min.	168	165	51	56	84
6	Smoke point, mm, max.	N.A.	N.A.	21	23	27.5
7	Aniline point, ^{0}C	94	95	75	77	84
8	Diesel index	37.2898	66.7114	72.8454	72.73	77.7887
9	CCR, wt%	4.17	4.59	0.0681	0.4807	0.50
10	Pour point, ^{0}C	N.A.	N.A.	– 2	18	22
11	Copper corrosion test (at 100^{0}C for feed and at 50^{0}C for product)	N.A.	N.A.	Not worse than no. 1	Not worse than no. 1	Not worse than no. 1
12	Acid value, mg of KOH/gm of sample	1.866	1.74	0.3414	0.7501	0.842

13	Saponification value, mg of KOH/gm of sample	9.13	4.7432	3.1672	3.1416	2.67
14	Refractive index	N.A.	N.A.	1.4507	1.4583	1.4905
15	Calorific value (kJ/gm)	35.4995	38.3487	42.1482	40.9862	37.7124
16	Water content	12.5% by Dean and Stark method	Traces by Dean and Stark method	0.034% 364 ppm by KF	0.044% 461 ppm by KF	0.069% 690 ppm by KF
17	ASTM % Recovery ↓	Temperature (^{0}C) →				
	IBP	-NA-	-NA-	99	116	154
	10%	-NA-	-NA-	182	191	204
	20%	-NA-	-NA-	204	260	266
	30%	-NA-	-NA-	252	264	291
	50%	-NA-	-NA-	296	320	329
	60%	-NA-	-NA-	330	360	362
	70%	-NA-	-NA-	354	368	372
	80%	-NA-	-NA-	361	378	390
	90%	-NA-	-NA-	372	N.A.	N.A.

1. Specific gravity and API gravity:
It is observed that the product specific gravity is less than the feed at all three temperatures. The specific gravity of product is in the order of 425 < 450 < 475^{0}C. This indicates that the product obtained at 425^{0}C is lighter than the product obtained at 450 and 475^{0}C. [2, 24, 25]

2. Viscosity and Flash Point:
The product obtained at 425^{0}C having less value for flash point and viscosity than the 450 and 475^{0}C. The order of increase in the flash point and viscosity is 425 < 450 < 475^{0}C. This indicates that the lower temperature cracking gives component having less viscosity and low flash point.[2, 24, 25]

3. Aniline Point:
The product at 425^{0}C having less aniline point than the 450 and 475^{0}C products. Thus product with temperature 425^{0}C gives comparatively more aromatics than the product with 450 and 475^{0}C. As saturated hydrocarbons having high aniline point is present in more quantity in 475^{0}C product.[2, 24, 25] The order of increase in aniline point of product is 425 < 450 < 475^{0}C.

4. CCR Value:
The CCR value for 475 and 450^{0}C is nearly close but product with 425^{0}C is very less. As low molecular hydrocarbon gives low CCR value[2, 24, 25] and hence 425^{0}C product having low value for CCR.

5. Smoke Point:
The order of increase in smoke point is 425 < 450 < 475^{0}C. Thus product obtained at 425^{0}C consists of comparatively more aromatic hydrocarbon[2, 24, 25] and as temperature of cracking increases saturated hydrocarbon in product steam increases.

6. Total Acid Value and Saponification Value:
Acid value shows the trend of decrease in values as temperature of cracking decreases. Whereas saponification value shows the trend of increase in values as temperature of cracking decreases. [2, 24, 25]
Decrease in acid value with decrease in temperature of cracking indicate that at lower temperature gives lighter product which associated with very less amount of acidic component, whereas more acidic component is associated with high molecular weight of hydrocarbon, which are present in high temperature, cracking product. Increase in saponification value with decrease in cracking temperature indicated that saponificating constituent is present in more quantity with lighter hydrocarbon which is obtained at 425^{0}C cracking.

7. ASTM Distillation:
This is the peculiar characteristics of hydrocarbon fuel sample. The product at 425^{0}C, gives ASTM distillation with low IBP and 50% distillating temperature than 450^{0}C and 475^{0}C, indicating that the pyrolysis temperature of 425^{0}C gives more lighter product than 450 and 475^{0}C.

V. MATERIAL BALANCE

Batch	Feed (in gm)	Cracked Product (in gm)	Residue (in gm)	Gases + Losses (in gm)	% Cracked Product
425^{0}C	830.08	618.25	137.67	74.16	83.41%
450^{0}C	843.36	661.35	143.93	38.08	82.93%
475^{0}C	834.69	660.66	142.61	31.42	82.91%

VI. CONCLUSION

From all these observations, it is confirmed that when COW waste after de-emulsification and dehydration, subjected to high temperature i.e. more than 400^{0}C, it undergoes cracking. Again the pyrolysis temperature of 425^{0}C gives more lighter product than the 450 and 475^{0}C. [2, 24, 25] This is evidence from specific gravity, viscosity, flash point and ASTM distillation tests. The pyrolysis of COW waste at 425^{0}C gives product with more aromatic hydrocarbon and less saturated (paraffinic) hydrocarbon, this is evidence from aniline point, smoke point and pour point test.

The material balance also indicates that pyrolysis at 425^{0}C gives slightly more cracked product.

Thus from all these, it can be concluded that the pyrolysis at 425^{0}C gives more lighter product with more aromatic hydrocarbons. This might be due to:

- The optimum temperature for COW waste cracking to obtained lighter hydrocarbon is 425^{0}C.
- At higher temperature, cracking might be higher (more depth of cracking), but it leads to give more secondary reactions. This gives more and more saturated products, due to combination and or addition reaction which, having high molecular weight than the primary product.

Common trends for hydrocarbon pyrolysis is that as temperature increases, depth of cracking increases, which able to give more and more lighter product. [2, 24, 25] But here product at 425^{0}C pyrolysis is lighter than the 450 and 475^{0}C. Thus for COW waste in this case optimum operating temperature for pyrolysis to yield lighter fuel is 425^{0}C. For further inspection or study the effect of temperature, the pyrolysis is to be carried out at lower possible temperature i.e. less than 425^{0}C.

ACKNOWLEDGEMENTS

1. Author wish to thank Shrirang Petrochemical Industry, Mumbai (M.S.), India for sponsoring and providing sample for this work.
2. Author also thankful to Department of Chemical Technology for providing laboratory facility for this research work.

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Selukar N. B. To Study the Effect of Temperature on Pyrolysis of Crude Oil Washing Waste." International Journal of Engineering Research and Applications (IJERA) , vol. 7, no. 11, 2017, pp. 18-22.