Indian Journal of Chemical Technology
Vol. 27, November 2020, pp. 521-524

Preparation of complex polyol ester base oil for lubricant from cyclohexane oxidation waste water

Ananta Kumar Mishra*, Mayur C Valodkar & Pujan B Vaishnav

Research & Development Centre, Gujarat State Fertilizers & Chemicals Ltd., Vadodara, Gujarat, India 391 750 India

E-mail: akmishra@gsfcltd.com

Received 10 October 2019; accepted 14 October 2020

Oxidation of cyclohexane in air produces cyclohexanone and **c**yclohexanol in cyclopol-bis process along with waste water stream containing valuable carboxylic acids. Process is devised in this manuscript to prepare complex polyol ester base oil by utilizing the waste water. The waste water stream from the cyclohexane oxidation process of Gujarat state fertilizers and chemicals ltd. has been vacuum distilled with a vacuum of 700 mmHg to remove water followed by filtration to separate the solid and liquid fractions. The liquid fraction is reacted with diethylene glycol to synthesize complex polyol ester base oil for lubricant. The base oil so obtained has a kinematic viscosity of 113 cSt at 40°C, pour point of -33°C and viscosity index of 109.

Keywords: Base oil, Cyclohexane oxidation, Cyclohexanone, Lubricant, Polyol ester

The waste water from chemical industries is the major source of air, water and land pollutions[1,2]. Hence, actions are being taken to minimize the pollution either by chemical or biological treatment or by incineration[3-10]. Cyclohexanone is of utmost demand among other chemicals due to its usage for the production of Caprolactam, Nylon-6 and Adipic acid. Air oxidation of cyclohexane leads to the production of cyclohexanone and **c**yclohexanol (popularly known as KA oil) as the main products via Cyclopol-bis process[11]. The rate of cyclohexane conversion is maintained between 4-6% during this process, to avoid by-product formation. However, it has been found that even at the mentioned conversion rate, the by-product formation cannot be avoided and it produces mixture of carboxylic acid and hydroxy acids. In this process, the oxidized product is washed with water to remove the impurities present, followed by the separation of organic phase from aqueous phase. The aqueous phase contains the mixture of carboxylic acid and hydroxy acids. The Caprolactam expansion plant of Gujarat state fertilizers and chemicals ltd (GSFC) produces approximately 100 MT per day of this waste water stream and it constitutes approximately 75-82% water and remaining organic acids and hydroxy acids. At present, the stream is being incinerated after certain processing steps at GSFC. The organic part of the stream mainly consists of Adipic acid, Glutaric acid, Succinic acid, 6-Hydroxy caproic acid, Butyric acid, Valeric acid, Caproic acid and other C-4 to C-6 complex hydroxy acids. Hence, the current stream under investigation can be a potential source of chemical products including Adipic acid and base oil for lubricant[12,13].

Base oil for lubricant can either be petroleum based or synthetic in nature. Synthetic base oils are prepared either from petroleum or from vegetable oil feedstock. Examples of synthetic base oils are (a) Polyalpha olefins, (b) Dibasic acid ester, (c) Polyol esters, (d) Alkylated aromatics, (e) Polyalkylene glycols and (f) Phosphate esters[14]. Polyol ester/ complex polyol ester base oil can be used as eco-friendly cutting oil[15], industrial lubricants[16], ozone friendly refrigerator compressor lubricant[14,17], etc. Polyol ester/ complex polyol ester base oil can be synthesized by the reaction of polyol with the organic acids. Many research work has already been done in this regard using different dicarboxylic acids such as fatty acids, Adipic acid, etc. and different polyols such as Neopentyl glycol, Pentaerythritol, 1,2-Propylene glycol, 1,4-Butanediol, etc.[18]. Beran[19] has also used similar stream to produce polyol ester base oil. However, the process involves reaction of acids with Pentaerythritol or Trimethylol propane by azeotropic distillation method using Toluene as the solvent.

Application of solvent makes this process difficult for commercialization due to handling of plenty of solvents along with their recovery cost. Hence, a simple process for the preparation of complex polyol ester has been described in the current investigation. For this purpose, the waste water from the Cyclohexane oxidation plant is concentrated and filtered. The filtrate obtained from the organic part was used as the source of carboxylic acid and diethylene glycol (DEG) was used as the source of hydroxyl group.

Experimental Section

The oxidation byproduct stream was obtained from GSFC Caprolactam expansion plant. DEG (98.5% pure) was purchased from Molychem and used without further purification. Sulphuric acid (98%) was obtained from GSFC. Sodium hydroxide pellets obtained from Merck was diluted with water to make it 5% solution.

Synthesis of polyol ester

The acidic waste water from the Cyclohexane oxidation process was distilled at 70°C under vacuum (700 mmHg) in a round bottomed flask to remove water. The viscous waxy material so obtained was then filtered under vacuum (700 mmHg) to separate the solid (residue) and liquid parts (filtrate). The COOH content of the filtrate so obtained was calculated with respect to mg KOH/g of sample. Based on that, calculated amount of DEG was added. The mixture was heated under vacuum (700 mmHg) at 110°C for 4 h in presence of sulphuric acid (98%) as catalyst. It was thoroughly washed with water and the aqueous and organic layer were separated. The organic layer was collected and analyzed as Base oil.

Characterization

The lubricant obtained was characterized using viscosity at 40 & 100°C (procedure IP: 71/80), viscosity index (procedure IP: 226/80), pour point (procedure IP: 15/67), neutralization value (procedure IP: 177/64) and density by standard method of weight by volume process.

Results and Discussion

The waste water obtained from Caprolactam expansion plant of GSFC has the tentative composition as mentioned in Table 1 (analyzed by HPLC method). Among these acids, dicarboxylic acids such as Adipic acid, Glutaric acid, Succinic acid and 6-Hydroxy caproic acid are solid in nature whereas, monocarboxylic acids such as Caproic acid, Valeric acid, Butyric acid and complex hydroxy acids with low molecular weight are liquid in nature. The liquid carboxylic acids when reacted with diol or polyol gives rise to polyol ester which can be used as base oil for lubricant[19,20].

Table 1 —Tentative composition of the byproduct stream obtained from GSFC caprolactam expansion plant

Component	Approximate Content (%)
Adipic Acid	2-3
Glutaric Acid	2-3
Succinic Acid	2-3
Butyric Acid	4-5
Caproic Acid	4-5
Valeric Acid	5-6
Cyclohexyl hydroperoxide	4-6
Water	75-82
Others	1-3

In this study, the waste water is evaporated to remove water completely to obtain a waxy material (containing organic carboxylic acids and hydroxy acids). It was then filtered and the residue obtained was used for the extraction of Adipic acid, whereas the filtrate was used as the source of carboxylic acid for the preparation of base oil for lubricant. The extraction process of Adipic acid from this stream is sent for publication elsewhere and this manuscript will deal only with the process for the preparation of Base oil for lubricant from the filtrate.

The filtrate, when reacted with Trimethylolpropane or with Pentaerythritol (as mentioned by Beran[19]), gelly mass was obtained. This may be due to the presence of complex hydroxy acids in the filtrate. The purpose of this study was not to utilize only the monocarboxylic acid but to utilize the whole filtrate. Hence, DEG was used as the source of hydroxyl group and sulphuric acid (98%) was used as the catalyst. The progress of the reaction was monitored by the water removed as distillate during the course of reaction. Once the water stops coming out as distillate, the reaction was stopped. The reaction mass was washed with water and organic layer was separated and analyzed (Table 2). The product obtained by this process is named as Base oil-1 afterwards in this manuscript. As mentioned in Table 1, the viscosity at 40 and 100°C are 52.5 and 8.7 cSt, respectively which is good enough for many applications. The viscosity index which is a measure of change in viscosity with respect to temperature is 133. This suggests that the viscosity of Base oil-1 is

Table 2 —Properties of Base oil-1

Properties	Base oil-1
Kinematic viscosity @ 40 deg C (cSt)	52.5
Kinematic viscosity @ 100 deg C (cSt)	8.7
Viscosity index	133
Pour point deg C	-18
Flash point deg C	168
Water content, ppm	20
Total acid number mgKOH/g (TAN value)	0.79
Density (g/cc)	1.07

Table 3 —Properties of Base oil-2

Properties	Base oil-2
Kinematic viscosity @ 40 deg C (cSt)	113
Kinematic viscosity @ 100 deg C (cSt)	13
Viscosity index	109
Pour point deg C	-33
Flash point deg C	175
Water content, ppm	20
Total acid number mgKOH/g (TAN value)	0.02
Density (g/cc)	1.15

not much affected with the change in temperature. The hydroxyl number of Base oil 1 is found to be 160 mg KOH/g of sample. The flash point which is very important for any kind of applications is found to be 168°C and is slightly lower. The acidity (0.79 mg KOH/g) of the Base oil-1 is also poor for any application. Hence, the process for the preparation of Base oil was modified in the second process.

In the second process, the filtrate from the waxy carboxylic acid mixture (obtained after water evaporation of the stream) was distilled at 160°C till the low volatile organics ceased to come out of the reaction mass. It was then reacted with DEG in a similar manner as described earlier in the experimental section. After complete removal of water from the reaction medium, the unreacted acid in the system was neutralized using 5% NaOH solution. Afterwards aqueous and organic layers were separated by a separating funnel. The resulting organic layer (named as Base oil-2 afterwards in this manuscript) was analyzed and the results are mentioned in Table 3. It can be seen that the kinematic viscosity at 40°C of Base oil-2 increased to 113 cSt compared to 52.5 cSt for Base oil-1. However, the viscosity index decreased slightly from 133 to 109 and the pour point further reduced to -33°C. The TAN value increased to 0.02 mgKOH/g compared to 0.79 mg KOH/g for Base oil-1. Similar to the viscosity, the density of Base oil-2 also increased to 1.15 g/cc compared to 1.07 g/cc for Base oil-1. Due to the removal of low volatile organic acids from the filtrate, the flash point of Base oil-2 was obtained as 175°C compared to 168°C for Base oil-1. The hydroxyl number of Base oil 1 is found to be 150 mg KOH/g of sample. This is due to the decrease in the low molecular weight volatile components. Several other methods were also tried in laboratory to improve the flash point of the base oil further but without any success. Hence, it can be concluded that the flash point of the Base oil depends on the type of starting material (carboxylic acid moiety) present on the effluent stream. This base oil can be utilized where high viscosity and low pour point and low flash point are required. Highly viscous complex polyol ester base oil with very good pour point and viscosity index could be obtained from the Cyclohexane oxidation byproduct stream by this process. This will greatly reduce the carbon foot print generated due to incineration of the stream.

Conclusion

A process was devised to reduce the carbon footprint from the environment by completely utilizing the waste water generated from Cyclohexane oxidation plant. The waste water stream from Caprolactam expansion plant of GSFC was used for the preparation of Adipic acid and complex polyol ester Base oil. The water from the stream was evaporated followed by filtration. The filtrate so obtained was reacted with diethylene glycol (DEG) to obtain Base oil for lubricant. In the first process the filtrate as a whole was reacted with DEG but the Base oil so produced was having low flash point (168°C) and acidity of 0.79%. In order to improve the flash point of the base oil, the low volatile organic acids were distilled out from the filtrate and afterwards reacted with DEG to obtain base oil with flash point of 175°C. Nutralization of the base oil with 5% NaOH solution led to lower acidity of the final product. The process mentioned in this manuscript can be extended to similar streams obtained from other cyclohexane oxidation plants.

Acknowledgement

The authors thank GSFC Ltd. for sponsoring our research work and providing byproduct stream from caprolactam expansion plant. Authors also acknowledge the contribution of Mr. N K Sanchapara during this work.

References

1 Bhatnagar A & Minocha A K, *Indian J Chem Technol*, 13 (2006) 203.
2 Nasr F A, Doma H S, Abdel-Halim H S, El-Shafai S A, *Environmentalist*, 27 (2007) 275.
3 Hu H Y, Goto N & Fujie K, *Water Sci Technol*, 10 (1999) 9.
4 Alvarez D, Garrido N, Sans R & Carreras I, *J Cleaner Production*, 12 (2004) 781.
5 Awaleh M O & Soubaneh Y D, *Hydrol Current Res*, 5 (2014) 1.
6 Meenachi S & Kandasamy S, *Indian J Chem Technol*, 24 (2017) 630.
7 Gaouar Yadi M, Tizaoui K, Gaouar Benyelles N & Benguella B, *Indian J Chem Technol*, 23 (2016) 204.
8 Singh I B & Chaturvedi K, *Indian J Chem Technol*, 22 (2015) 162.
9 Chakradhar B & Shrivastava S, *Indian J Chem Technol*, 11 (2004) 617.
10 Dhale A D & Mahajani V V, *Indian J Chem Technol*, 7 (2000) 11.
11 Gruszka M, Malinowski T, Rygiel S & Wais J, *Chemik*, 66 (2012) 1083.
12 Kurowski G, Vogt O & Ogonowski J, *Chemik*, 70 (2016) 99.
13 Mehta K J, Varshney A K, Siddiqui M A & Mehta M H, *Chem Eng World*, 24 (1989) 63.
14 Wu M M, Ho S C & Forbus R, Synthetic Lubricant Base Stock Processes and Products; In book: *Practical Advances in Petroleum Processing*, (2006) 105.
15 Bisht R P S, Kaul S, Nagendramma P, Bhatia V K & Gupta A K, *J Synth Lubrication*, 19 (2002) 243.
16 Lubrizol Corp, *U S Pat* 7, 662, 758 B2, 13 June 2006.
17 Chemtura Corp, *U S Pat* 8, 865, 015 B2, 9 Oct 2012.
18 Dow Global Technol, *W O Pat* 129, 292 Al 22 Oct 2009.
19 Beran E, *J Synth Lubrication* 18 (2001) 39.
20 Archer-Daniels-Midland Company, *U S Pat* 7,126,018 B2, 24 Oct 2006.