

## Study of Catalyst and Co- Catalyst Effect on Preparation of Lubricant from Heavy Propylene Tetramer (HPT)

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### ABSTRACT

In this research we used Heavy Propylene Tetramer (HPT) and  $AlCl_3 - BF_3$  (Lewis acids) as catalyst and ethanol, n-propanol and n-butanol as co-catalyst. Using Lewis acids as catalyst, the HPTs form molecules with higher molecular weight. Since the raw materials of the reaction are by products of other reactions, are not pure and contain various compounds with different M.W and also different chemical and physical properties. This fact affects catalyst weight ratio which must be applied for a better result.

The effect of different catalysts and co-catalysts on yielded lubricant and reaction yield is investigated. The results show that using alcohol with higher M.W as co- catalyst, increases reaction yield and iodine number, and also a better lubricant can be obtained. Also,  $AlCl_3$  seems to be a better catalyst in laboratory scale research comparing to  $BF_3$ .

**Keywords:** Propylene Oligomer; Heavy Propylene Tetramer; Catalysts; Co-Catalyst

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### INTRODUCTION

A lubricant is a substance introduced between two moving surfaces to reduce the friction and wear between them. A lubricant provides a protective film which allows for two touching surfaces to be separated and "smoothed," thus lessening the friction between them. Lubricants chemically interact with all surfaces so that contact only occurs with the smooth and free lubricant [1]. By this process, abrasive particles are dissolved into the lubricant, thus making them also very good solvents and cleaners.

Petroleum-based lubricants like Vaseline tend to dissolve petroleum products such as rubber and plastic, while water-based lubricants tend to dissolve polar chemicals; hence the additives.

The lubricant must be replaced when it has dissolved to saturation, because the inability to dissolve additional abrasive debris allows abrasive particles to scrape against or become lodge in the working surfaces, thus introducing a margin for physical contact between them. Lubricants which dissolve working surfaces (like the petroleum products Vaseline with rubber) defeat their purpose by corroding the smooth surfaces by their own dissolving power, thus compromising structural integrity, surface smoothness, and system-wide contamination [2]. One of the single largest applications for lubricants, in the form of motor oil, is to protect the internal combustion engines in motor vehicles and powered equipment [3].

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Problems related to engines lubrication in industries are not completely solved yet. There are many materials like synthetic poly olefins which are used as lubricant. In recent years synthetic oils have attracted much attention, because of their better properties like viscosity, in compare to inorganic oils. Yet, since the synthetic oils can not afford all the needs completely, various additives for investigating the effects on the oil properties have been used. Although synthetic lubricants show better properties, they are much more expensive than inorganic ones.

Propylene polymerization yields oils with average viscosity index (VI) and low heat-stability. Controlling such reactions, results in products with various viscosity and VT [4]. AlCl<sub>3</sub> with HBr or BF<sub>3</sub> in chloride hydrocarbons act as catalyst. Co polymers which are obtained from different molar ratio of ether and propylene are of great importance [4]. VI of these products is about 140 and their pour point is approximately -54 °C. And shows a good heat-stability and resistance against oxidation. Olefins polymerization with high molecular weight yields oils which have proper uses in industry. Olefins which are obtained from natural cracking of paraffin are used as raw material [4].

VT of obtained heavy olefins depends on primary olefins. Branched alpha olefins have lower VI than straight chain molecules. N multi step polymerization, oligomerization of primary olefins is done with acidic catalysts (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>), in the second step, Friedel-Crafts catalyst is used. Low stability and low resistance against oxidation of poly olefin oils, is related to polymers double bonds. The unsaturated bonds are removed by hydrogenation or reaction with iso-paraffin [4].

## MATERIALS AND METHODS

### General

Propylene Oligomer (Heavy Propylene Tetramer (HPT), (number of carbon in this compound 5-8) is taken from Abadan Petroleum Complex. In Table 1, summarized some properties of heavy propylene tetramer (HPT). Materials which are used as catalyst have the specification mentioned below:

AlCl<sub>3</sub> from Merck Company, with purity 99.99%. Some properties for this material are shown in table 2; BF<sub>3</sub> were prepared from Merck Company, with purity 99.95%. Ethanol, n-Propanol and n-Butanol used as Co-catalyst, were produced by Merck Company, with purity 99.99%.

**Table1.** Some Properties of Heavy Propylene Tetramer

Specification	Heavy Propylene Tetramer
Specific Gravimeter at 15.6°C	0.8778
Total Sulfur (wt %)	0.03
Flash Point (760 mmHg)	108
Colour (ASTM-D1500)	7.5
Copper Corrosion (3 hr at 100°C)	1a

**Table 2.** Some Properties of Aluminum Chloride

Molecular Weight	133.4 g/mol
Melting Point	180°C
Solubility in water(20°C)	450 (g/Lit)
pH (20°C)	2.4

### Preparation of propylene oligomer using different catalysts

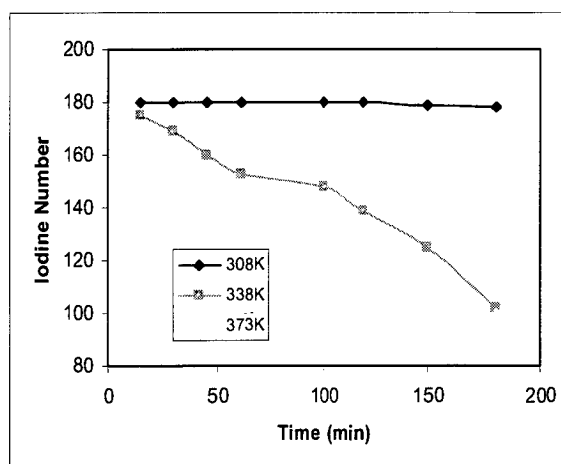
The mixture (HPT, catalysts and co-catalysts) is washed by sodium carbonate solution; it removes the catalyst off the mixture. The product is then distilled in order to obtain the pure product. The same procedure, such as HPT with catalysts is used for AlCl<sub>3</sub> and another catalyst. Measuring the Iodine Number is order according Ref. [6]. HCl is also mixture to provide H<sup>+</sup> and make an acidic medium. To measure the relations yield, the mixture should be first, distilled. It separates a used reactant from the produce of reaction. The reaction yield is measured using weight percentage ratio of product to reactant [7].

### Preparation of HPT using Co-Catalyst:

All steps are take the procedure described above, but ethanol, n-propanol and n-butanol are added in certain amount as co-catalyst [8].

## RESULT AND DISCUSSION

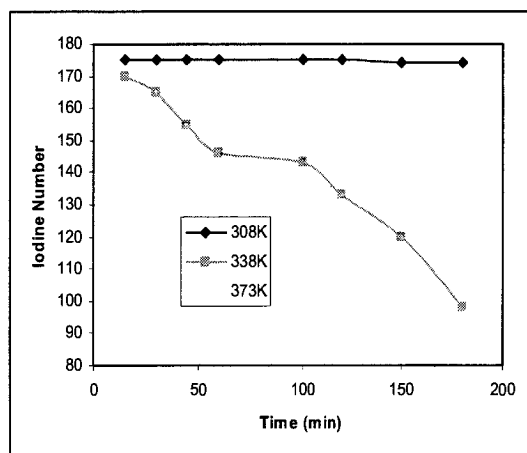
Figures 1 and 2 show the changes of Iodine Number with time, when BF<sub>3</sub> and AlCl<sub>3</sub> are catalyst respectively.



**Figure 1.** A change of Iodine Number with time. HPT 10g, catalyst BF<sub>3</sub> 2g, Co-Catalysis Ethanol 1 g.

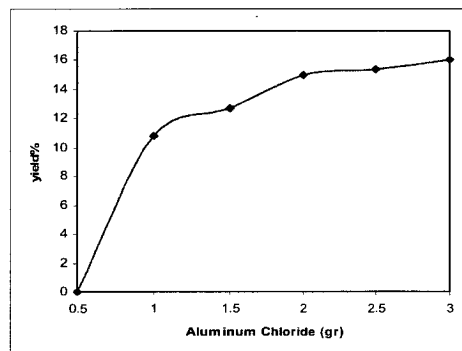
The iodine number (or "iodine adsorption value") in chemistry is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. An iodine solution is yellow/brown in color and any chemical group in the substance that reacts with iodine will make the color disappear at a precise concentration. The amount of iodine solution thus required to keep the solution yellow/brown is a measure of the amount of iodine sensitive reactive groups. One application of the iodine number is the determination of saturation of hydrocarbon as double bonds in hydrocarbon, also react with iodine compounds. The higher the iodine number, the more unsaturated hydrocarbon bonds are present in a hydrocarbon [9]. In a typical procedure the Iodine Number is lower when AlCl<sub>3</sub> is used; therefore it is used in the main procedure. At this section 10g of HPT is used, the amount of BF<sub>3</sub> and AlCl<sub>3</sub> is 2g, and 1 g ethanol was used as Co-Catalyst [10].

For a simple analysis, 0.2 grams of product is mixed with 10mL 1,1,1-trichloroethane. It is then left in the dark for 30mins. Next, 15mL of 10% potassium iodide solution and 10mL of deionised water is added. This is then titrated against 0.1M sodium thiosulfate solution. 1mL of 0.1M sodium thiosulphate solution is equal 0.01269g of iodine. The difference between a control titration and the product titration with the hydrocarbon present multiplied by this factor gives the mass of iodine, absorbed by the hydrocarbon [10].

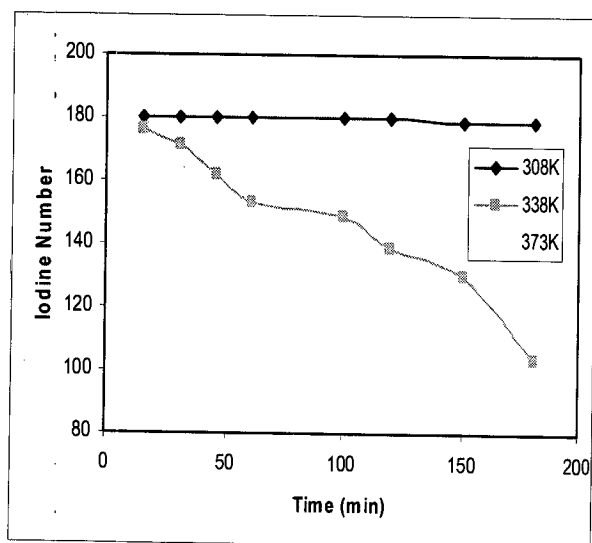


**Figure 2.** A change of Iodine Number with time. HPT 10g, catalyst AlCl<sub>3</sub> 2g, Co-Catalysis Ethanol 1 g.

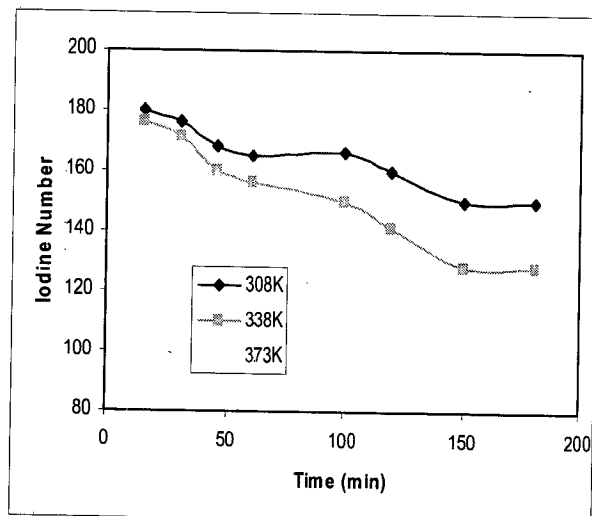
Three alcohols were used: ethanol, n-propanol and n-butanol. The reaction of HPT with Aluminum Chloride (as catalyst) and alcohol (as co-catalyst) is Also BF<sub>3</sub> have gas state, therefore we used diethyl ether. The more amounts of the catalyst, the more reaction yield and the less Iodine Number. Yet, reducing the amount of AlCl<sub>3</sub> to 0.5 g for 20 g of reactant in 308K causes the reaction stops. Also, increasing the catalyst from 2 to 3 g does not make any noticeable increase in the reaction yield. This point is shown in Figure 3. At this section we study the effect of Aluminum Chloride amount as catalyst on the reaction yield. The amount of co-catalyst is 1.0 g for n-butanol. When the amount of Aluminum Chloride is 0.5g, the yield of reaction is 0%, because the amount of Aluminum Chloride is very low [11]. When 2 and 3 g of Aluminum Chloride was used, the yield of reaction increases.



**Figure 3.** Reaction yield HPT with Amount of Aluminum Chloride for catalyst, Co-catalysis n-butanol 1.0 g.



**Figure 4.** A change of Iodine Number with time. HPT 10g, catalyst AlCl<sub>3</sub> 2g, Co-Catalysis n-butanol 0.6 g.



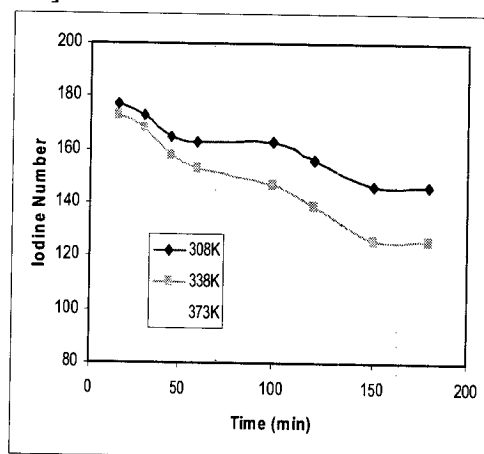
**Figure 5.** A change of Iodine Number with time. HPT 10g, catalyst AlCl<sub>3</sub> 2g, Co-Catalysis n-butanol 1.0.

In order to reach a better result of the reaction when Aluminum Chloride is used as catalyst, three alcohols were examined as co-catalyst: ethanol, n- propanol and n-butanol. A lubricant will be produced when AlCl<sub>3</sub> and an alcohol were used as catalyst and co-catalyst respectively [12].

**Table 3.** Reaction yield HPT with, ethanol (1g), n-propanol (1g) and n-butanol (1g) for Co-catalysis

Co-catalysis	Reaction yield%
ethanol	20.19%
n-propanol	27.41%
n-butanol	29.31%

When the yields of reactions are equal, the Iodine Number of the product, obtained in lower temperature is lower. As the temperature increases, Iodine Number increases. Also an increase in the co-catalyst from 0.6g to 1.4g results is a decrease in the Iodine Number. The result is in agreement with prior experiments [13-18].



**Figure 6.** A change of Iodine Number with time. HPT 10g, catalyst AlCl<sub>3</sub> 2g, Co-Catalysis n-butanol 1.4 g.

## CONCLUSION

It can be concluded that AlCl<sub>3</sub> is a good alternate as catalyst among Aluminum halides and n-butanol can be used as a proper co catalyst. The reaction is better to be run in the temperature lower than 373K. It produces products with lower Iodine Number and higher yields.

## ACKNOWLEDGMENTS

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