International Journal of Engineering Applied Sciences and Technology, 2017
Vol. 2, Issue 4, ISSN No. 2455-2143, Pages 121-126
Published Online February-March 2017 in IJEAST (http://www.ijeast.com)

INSIGHT OF OLEFIN COPOLYMER PROCESSES

Arya Bhardwaj
Dept. of Petrochem & Petroleum Refinery Engineering
Punjab Technical University,
Jalandhar, Punjab, India

Abstract - Novel copolymers of α – olefins comprised of intramolecularly hetrogeneous and intermolecularly homogeneous copolymer chains. E – P copolymer oils containing ethylene, are known for their high viscosity index, low pour point and high stability. The olefins are polymerized in the presence of a catalyst formed by mixing a vanadium com• pound such as a vanadium halide, oxyhalide, or alkoxide with an organo-aluminum compound such as a trialkyl aluminum, alkyl aluminum hydride, or alkyl aluminumhalide. Ethylene is copolylmerized with a polyene under pressure with a vanadium catalyst to form amorphous vulcanizable elastomers, the vanadium compound content of said polymer is reduced and the color of the polymer improved by contacting at a higher pressure a polymerization effluent containing the ethylene copolymer and vanadium catalyst With a low molecular weight alcohol or ketone and thereafter washing this mixture under pressure with hydrocarbon or water to remove the residual vanadium compound.

I. INTRODUCTION

Olefin copolymer is an amorphous polymer comprised of ethylene & propylene which acts as a viscosity improver additive for oleaginous compositions such as lubricating & fuel oil compositions. Basically, these copolymers reduce SSI (Shear Stability Index) & molecular weight which acts as an improvement for the additive[8]. These copolymers in the mixture acts as a starting point material for the degraded copolymers which are prepared by co- polymerization processes with well-known catalyst system[9]. They may have broad and narrow molecular weight distributions with compositions of uniform polymer chains or alternatively, segmented copolymer chains which are intermolecularly homogeneous and intramolecularly heterogeneous. The mixture of degraded co-polymers is directly used as viscosity index improver additive. The degraded and undegraded co-polymers are grafted with grafting materials to enhance the properties and creating them useful as multifunctional viscosity index improver additive[1].

In "Polymerization of ethylene and propylene to amorphous copolymers with catalysts of vanadium oxychloride and alkyl aluminum halides". The use of a tubular reactor to produce ethylene-propylene copolymer is disclosed in which the composition varies along the chain length. More specifically, this reference discloses the production in a tubular reactor of amorphous ethylene- propylene copolymers using Ziegler catalysts prepared from vanadium compound and aluminum alkyl. ethylene and propylene useful for many purposes, and particularly to new synthetic lubricating oils having viscosity indexes, high oxidation, shear and thermal stabilities, and low pour points, these properties being possessed not only by the overall oil, but also by its fractions. . The basic process comprises adding ethylene and propylene and optionally a diene to a liquid hydrocarbon solvent containing a catalytic amount of a reaction product[7].

International Journal of Engineering Applied Sciences and Technology, 2017
Vol. 2, Issue 4, ISSN No. 2455-2143, Pages 121-126
Published Online February-March 2017 in IJEAST (http://www.ijeast.com)

II. PROCESSES

Patent – I

US4540753

This invention assigned to Exxon Research & Engineering Co., is related to novel copolymers of alfa – olefins. Basically, it relates novel copolymers of ethylene with other alfa – olefins comprised of copolymer chains with compositions which are intramolecularly heterogeneous and intermolecularly homogeneous. These copolymers are used in lube oil and elastomer. These processes are carried out in a mix – free reactor systems, which one where no mixing occurs between the portions of the reaction mixture that contains polymer chains initiated at different times [1]. The described reactors in the invention are as follows:

- Continuous Flow Stirred Tank Reactor (C.F.S.T.R): In a continuous flow stirred tank reactor, reactants and products are continuously added and withdrawn.
- Tubular reactors: It is a well known reactor which is designed to minimize mixing of the reactants in the direction of flow.

The catalyst used is Ziegler Natta Catalyst (VCl4) and co- catalyst is Tri Ethyl Aluminium Sesqui-chloride (Al2Et3Cl3) and premixing temperature is about $25^{o} – 40^{o}$[3].

P&FD for the process:

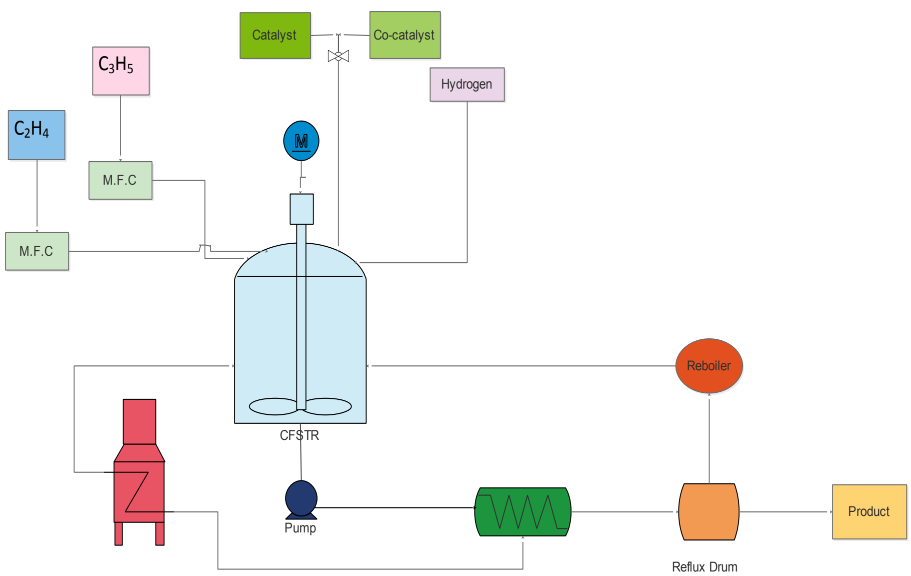


Figure3: Process Design

The following steps are:

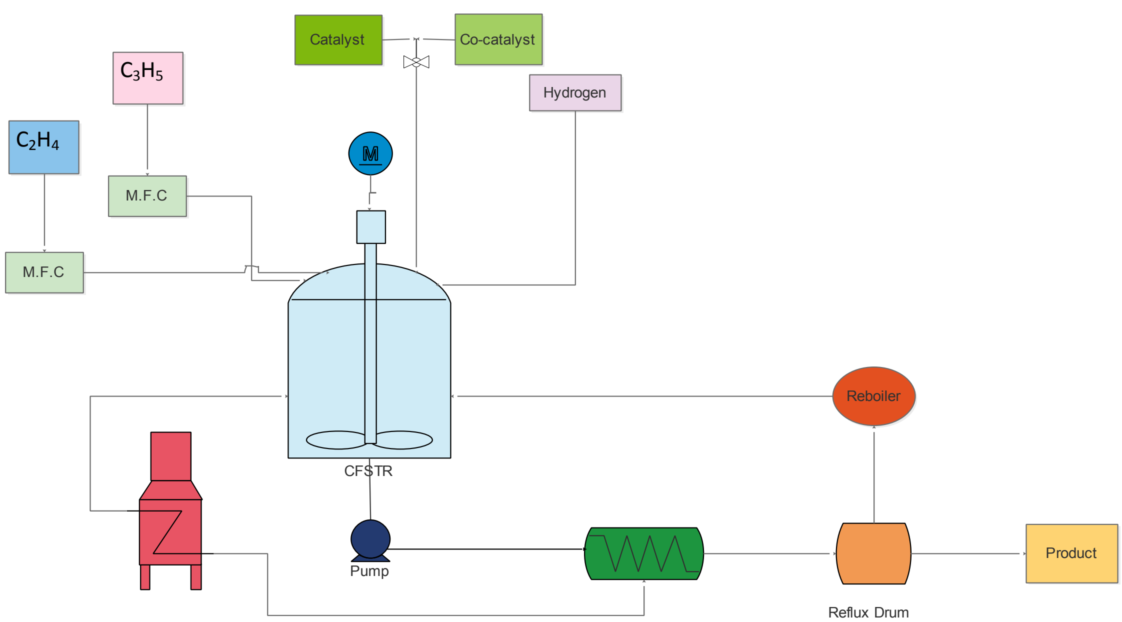
International Journal of Engineering Applied Sciences and Technology, 2017
Vol. 2, Issue 4, ISSN No. 2455-2143, Pages 121-126
Published Online February-March 2017 in IJEAST (http://www.ijeast.com)

- Firstly purge solvent in the reactor.
- Now charge, Feed (H2→C2→H2→C3) in sequence.
- Pressurize the reactor.
- Start charging catalyst and co-catalyst simultaneously.
- Now, the process will consume time which is known as Residence time

Patent – II

US 3851011

This invention assigned to Sun Research & Development Co., relates generally to new oily copolymers of ethylene and propylene useful for many purposes, an particularly to new synthetic lubricating oils having viscosity indexes, high oxidation, shear and thermal stabilities, and low pour points, these properties being possessed not only by the overall oil, but also by its fractions. Basically, this invention relates to the preparation of such oily copolymers through particular types of catalyst systems under defined conditions. It's a process for preparing a synthetic copolymer oil which comprises of propylene and ethylene in solution at a temperature range of 0° - 125°C. The reactor used in the described process is Continuous Stirred Reactor (C.S.T.R) with (VCl_4) as the catalyst and triethyl- sesquichloride ($Al_2Et_3Cl_3$) as co-catalyst[4].



P&FD for the process:

Figure 4: Process Design

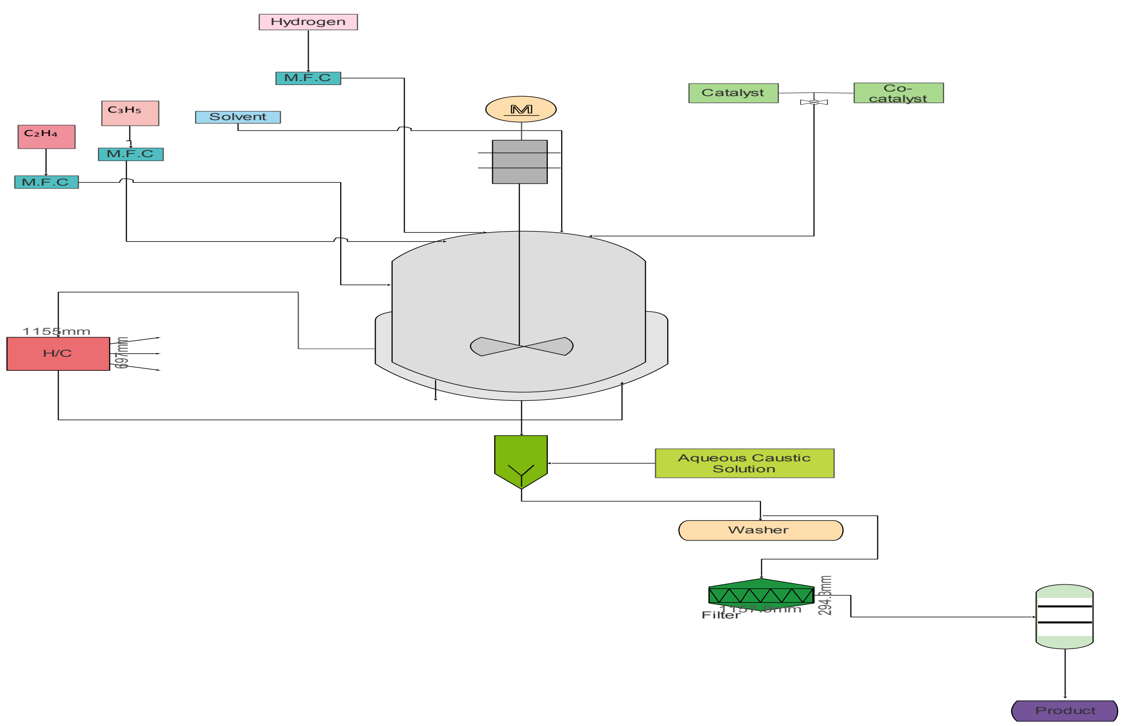
International Journal of Engineering Applied Sciences and Technology, 2017
Vol. 2, Issue 4, ISSN No. 2455-2143, Pages 121-126
Published Online February-March 2017 in IJEAST (http://www.ijeast.com)

- Firstly purge Solvent in.
- Now charge, Feed (H2→C2→H2→C3) in sequence.
- Pressurize the reactor.
- Start charging catalyst and co-catalyst simultaneously.
- Now, the process will consume time which is known as Residence time.
- Solvent is flushed from the reactor.
- Now, catalyst killer is used for killing the catalyst by solution of aqueous ammonia.
- Filtration is performed to separate out the solids remaining in the effluent.
- Distillation is performed to get yield.

Patent – III

US 3804815

The present invention assigned to Ethyl Corporation, is an improvement in the known process for producing ethylene-propylene copolymers or ethylene-propylene-diene terpolymers by reacting ethylene and propylene and optionally a diene in an inert solvent in the presence of a catalyst formed by mixing a vanadium compound with an organo-aluminum compound. In the improvement the vanadium and aluminum ash in the final product is reduced by washing the polymer solution with aqueous caustic, passing the washed hazy product through a filter, and removing the aqueous phase which separates as a result of the filter treatment, leaving a bright, clear, low ash polymer cement. The reactor system used in the present invention is Continuous Stirred Tank Reactor (C.S.T.R) with (VCl4) as the catalyst and tri-ethylaluminium $Al(C_2H_5)_3$.



P&FD of the process:

Figure 5: Process Design

International Journal of Engineering Applied Sciences and Technology, 2017
Vol. 2, Issue 4, ISSN No. 2455-2143, Pages 121-126
Published Online February-March 2017 in IJEAST (http://www.ijeast.com)

- Mixing the reaction solution of copolymer or terpolymer containing the catalyst residue with an aqueous caustic solution.
- Separating the spent aqueous caustic from the washed copolymer or terpolymer solution.
- Passing the washed solution through a filter.
- Removing the aqueous phase which separates from the filtered copolymer or terpolymer solution.

Patent – IV

US 363100

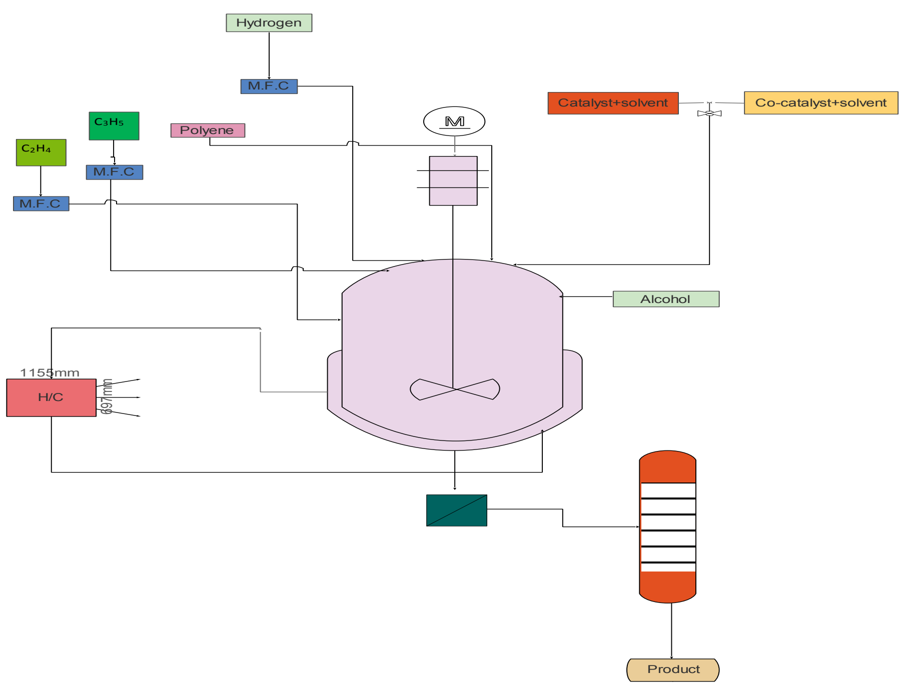
This invention assigned to B.F. Goodrich Company, relates generally to polymerization of ethylene, propylene and a polyene, polymerized in the presence of a reduced vanadium catalyst, that if after the polymerization reaction the polymerization mixture is contacted with a catalyst deactivator as an alcohol or ketone and then washed while maintaining ethylene in, and pressure on, the mixture greater than the pressure under which the polymerization was conducted, that the residual vanadium compounds remaining in the resulting copolymer are readily reduced to less than 100,the resulting copolymers are substantially colorless. The reactor system used in the present invention is Continuous Stirred Tank Reactor (C.S.T.R) with (VCl4) as the catalyst and Tri Ethyl Aluminium Sesique Chloride (Al2Et3Cl3). The reactor working conditions are:

Pressure: 25 – 100 psi, Temperature: -80^{o} - 25^{o}C, Catalyst Deactivator: Alcohol & Aqueous Caustic.

P&FD for the process:

Figure 6: Process Design

- Firstly, purge Solvent in.



- Now charge, Feed (H2→C2→H2→C3) with polyene in sequence.
- Pressurize the reactor.

- Start charging catalyst and co-catalyst with a mixture of solvent simultaneously.
- Now, the process will consume time which is known as Residence time.
- Hydrogen is added frequently in parts to control the M.W.D (Molecular Weight Distribution).
- Now, Alcohol is added to slow down the reaction.
- Effluent & alcohol is washed by the aqueous caustic.
- At last the product is sent to storage tank.

III. CONCLUSION

Olefins are the backbone of the Petrochemical Industries. These are used in various kind of applications used in specific projects focused on polymer and co – polymers and manufacturing of lubricants and additives used in various fields.

In this review the Olefin Copolymers are in the limelight. So, the Olefin Copolymers is generally an amorphous polymer comprised of ethylene & propylene which acts as a viscosity improver additive for oleaginous compositions such as lubricating & fuel oil compositions. Basically, these copolymers reduce SSI (Shear Stability Index) & Molecular weight which acts as an improvement for the additive. " These copolymers in the mixture acts as a starting point material for the degraded copolymers which are prepared by co- polymerization processes with well known catalyst system"[10]. They may have broad and narrow molecular weight distributions with compositions of uniform polymer chains or alternatively, segmented co-polymer chains which are Intermolecularly homogeneous and intramolecularly heterogeneous. The mixture of degraded co-polymers are directly used as viscosity index improver additive. The degraded and undegraded co-polymers are grafted with grafting materials in order to enhance the properties and creating them useful as multifunctional viscosity index improver additive. This is known as Olefin Co-polymers.

The processes mentioned in this review are based on the methods of preparing the co polymers and removal of catalysts. So, basically the processes clearly states that the monomers are copolymerized by using different catalysts and co – catalysts. The process works according to the required residence time and concerned conditions of temperature and pressure. The molecular weight distribution is governed by the catalysts, co – catalysts and hydrogen.

Basically, the processes on the removal of catalysts states that the reaction effluent is mixed with an aqueous caustic solution and washed with itself and then filtered out in order to remove the solids formed in the effluent and at last the product is resulted.

IV. REFERENCES:

1. Lubricant Additives Chemistry and Applications, by Leslie R. Rudnick, Marcel Dekker, INC.
2. http://phx.corporateir.net/External.File?item=UGFyZW50SUQ9MTEwODYwfENoaWxkSUQ9LTF8VHlwZT0z&t=1.
3. Charles Cozewith, Westfield; Shiaw Ju, Edison; Gary W. VerStrate, Matawan, all of N.J., US4540753, Exxon Research & Engineering Co., Sep. 10, 1985.
4. Richard S. Streans, Malvern, Irl N. Duling, West Chester, David S. Gates, Swarthmore, US3851011, Sun Research & Development Co., Nov. 26. 1974.
5. L. PLONSKER, US3804815, Ethyl Corporation, Apr. 16, 1974.
6. Bart A, Diliddo, US3631007, B. F. Goodrich Company, Dec. 28, 1971.
7. Lubricant Additives Chemistry and Applications, by Leslie R. Rudnick, Marcel Dekker, INC. Page no: 167.
8. http://chem.libretexts.org/Core/Organic_Chemistry/Polymers/Copolymers.
9. https://lubrizol.com/Lubricant-and-Fuel-Additives/Viscosity-Modifiers.
10. http://chem.libretexts.org/Core/Organic_Chemistry/Polymers/Copolymers.