NeoPentyl Glycol (NPG): A Unique Multi Purpose Chemical

TECHNOLOGY

Dr. Chanchal Samanta
Manager (R&D)
BPCL

Introduction

Consumer durable products are essential part of our modern life. These products are produced from many important chemicals. Among these important chemicals, oxygen containing organic compounds such as alcohol (R-OH); ethers (R-O-R); ketones (R-CO-R); aldehydes (R-CO-H); carboxylic acids (R-COOH); esters (R-COO-R); acid anhydrides (R-CO-O-CO-R); amides (R-C(O)-NR2). (Where "R" is an organic group) are widely used as raw material in the synthesis of many advanced synthetic polymers and chemical substances.

Polyols (compounds with multiple hydroxylfunctional groups such diol (with two hydroxyl groups), triol (three hydroxyl groups) and tetrol (with four hydroxyl groups) are important class of oxygen containing organic compounds, widely used in the synthesis of various synthetic polymeric materials such as polyether polyols, polyurethanes and polyesters etc.

Neopentyl glycol (NPG): A Unique Chemical

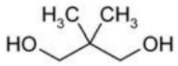
Neopentyl Glycol (NPG), IUPAC name 2,2-dimethyl-1,3-propanediol, CAS [126-30-7]) is an important diol which features unique chemical structure. NPG has two hydroxyl groups located in the 1, 3-position on the primary carbon atom. Additionally, it has two methyl groups instead of the usual two hydrogen atoms on the ?-carbon atom. This unique combination in the structure of NPG enablesrapid esterification, high chemical and thermal stability as well as high crystallinity and weatherability.

NPG: Properties and Applications

NPG is a white crystalline solid and partially soluble in water. It is soluble in oxygenated solvents and completely soluble in alcohols. A detailed chemical and physical property of NPG is provided in Table 1.

Neopentyl glycol is increasingly being used as an important chemical intermediate particularly in the manufacture of various synthetic resins, alkyd resins, polycarbonate resins, polyesters, paints, plasticizers, adhesives and synthetic lubricants. It is utilized by automotive industry, original equipment manufacturers (OEM), synthetic resin manufacturers and other plastic and polymer manufacturers. NPG is employed to enhance the stability of the polyester resin and increase its resistance against light, water, heat and chemicals to provide a longer product life. Synthetic lubricating esters produced through the esterification of NPG with fatty or carboxylic acids are found to be superior with respect to reduced potential for oxidation or hydrolysis, as compared to natural esters.

Table 1: Physical and Chemical properties of NPG (Source: Mitsubishi Gas Chemical)

Properties	Description
Appearance / Molecular weight	White solid,104.15 g/mol
Chemical Formula/ IUPAC Name	(CH3)2C(CH2OH)2/2,2-Dimethyl-1,3-propanediol
Chemical structure	
Melting point/Boiling point/Flash point	127 °C/208 °C
Solubility	Soluble in benzene, chloroform, highly soluble in ethanol, diethyl ether
Water Solubility	190g/100 ml at 20 0C (65%)
Thermal Stability	Pure NPG is thermally stable upto the boiling point. However, in the presence of alkali salts or bases, NPG decomposes above 140 0C. Thermal decomposition products: methanol, isobutanol, isobutyl aldehyde, formaldehyde etc.
Toxicity	Non-toxic to fish, Daphnids and Algae.
Stability & Reactivity	Stable. Incompatible with strong oxidizing agents, Acetic anhydride, Acid chlorides, Moisture. Combustible
Flash point/Ignition Temperature (°C)	129^0C /399^0C

NPG and its derivatives have the applications in the fields including water based coatings, magnetic coatings, gel coats, powder coatings, high solid systems, coil coatings, multilayer coatings (on alkyds, epoxy, polyester and poly urethane resins). It is also used as an intermediate for the synthesis of lubricants, plasticizers, adhesives, mortar or cement systems, photographic materials, pharmaceuticals, pesticides, fragrances, fibre lubricants antistatic agents, fabric softeners, vibration dampeners etc. A detailed sector wise application of NPG is provided in Fig 1.

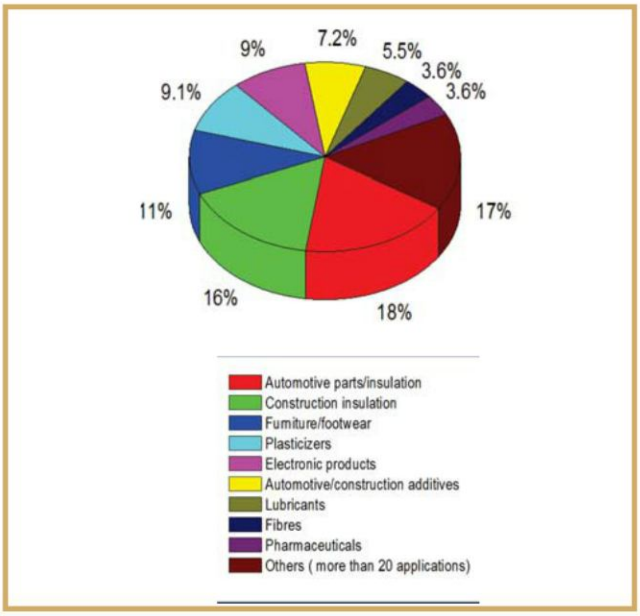


Fig1. Sector wise applications of NPG(Source: ICIS chemical Business report)

NPG has wide applications in coatings areas such as powder coatings based on NPG has improved impact and scratch resistance and high gloss. Synthetic lubricants made from NPG provide good lubricity and reduced corrosivity. It is also employed in enhancing the stability of the polyester resin and increases its resistance against light, water, heat and chemicals to provide a longer a product life.

The neopentyl glycol market is driven by its demand from polyester resins industry for a variety of coatings solutions. However, substitutability of neopentyl glycol(NPG) with ethylene glycol, a cheaper alternative, is expected to be the major restraining factor for the NPG market. New product applications in the pharmaceutical formulations could be a prospective market opportunity.

NPG: Worldwide Supply/Demand Scenario

Demand for NPG is rising steadily as market is driven by its demand from polyester resins industry for a variety of coating solution. The polyester resins manufactured from neopentyl glycol (NPG) find wide range of application is the automotive, construction, furniture, electronic, lubricants and plasticizer industries. According to consultancy firm TranTech report, global capacity of NPG was 485,000 tpa in 2005 while in 2015 it was around 800,000 tpa. Asper LGChem's, forecast, NPG production capacity in the world would be around 890,000 tpa by 2019 (Fig.2).

As per the forecast, production capacity of NPG in North America is expected to remain stable during the period of 2012-2019 while demand will increase marginally while in Europe during the same period, the supply will stood nearly steady. China will be the major drivers for NPG demand and supply (Fig.3). The projected installed capacity for NPG in China will increase by double during 2012-2019. While in rest of the Asia, the capacity will increase from 170,000 tpa to 220,000tpa during the same period. China's NPG demand growth rate to be 10% per annum during 2012-2019, while in Europe and America' demand it would remain around 4.0 % per annum. The Africa, Oceania and Middle East are also going to use more NPG in coming years and will see around 6.6% growth rate for NPG uses.

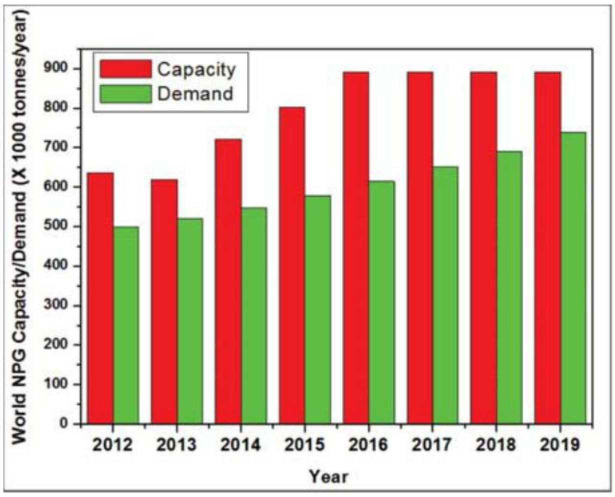


Fig 2. Worldwide current and future installed production capacity and demand of NPG in different regions (Source: LG Chem)

China and India, world's two most populous countries, will drive demand for consumer goods such as furniture, footwear, electronic products, automotives, pharmaceuticals, etc., which in turn will lead to further demand for NPG used in these products. Europe is the second largest consumer of neopentyl glycol (NPG), especially in the automotive and OEM sector. The demand for NPG is also driven by high use of polyester resins in powder coatings. North America is another major consumer for neopentyl glycol (NPG) due to its demand for synthetic lubricants and plasticizer industry. In Rest of the World, Brazil, Argentina and South Africa contribute to major demand for the market.

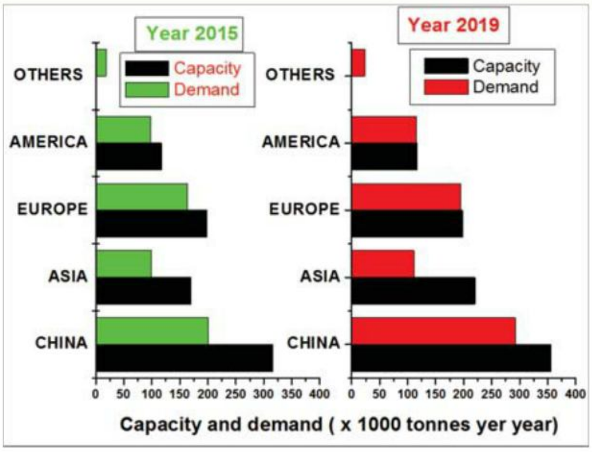


Fig 3. Region wise capacity and demand for NPG(Source: LG Chem)

Chemistry of NPG ProductionProcess

NPG is synthesized from formaldehyde and isobutyraldehyde. There are two main industrial production technologies: (1)Cannizzaro process technology and (2) Aldol condensation followed by hydrogenation technology. The advanced NPG production process is based on aldol condensation followed by hydrogenation, which is discussed in more details in the following section.

Production by Cannizzaro Reaction

A significant portion of the NPG produced commercially is synthesized by the combination of aldol condensation and a crossed Cannizzaro reaction (named after its discoverer Stanislao Cannizzaro) with either NaOH or Ca(OH)2 catalyst (Fig.4).

In aforementioned process, advantage is being taken of the fact that all -hydrogen atoms of the aldehyde i.e isobutyraldehyde react with formaldehyde in an aldol condensation. In a subsequent crossed-Cannizzaro reaction, the aldehyde group in the intermediate product hydroxypivaldehyde, CAS [597-31-9], is then reduced to alcohol with excess formaldehyde. The major benefits of the process arises from the fact that self-aldol of isobutyraldehyde requires a base stronger than OH- ions to occur to a significant extent, a relatively small excess of formaldehyde is sufficient for high conversion and a selectivity greater than 90% is achieved.

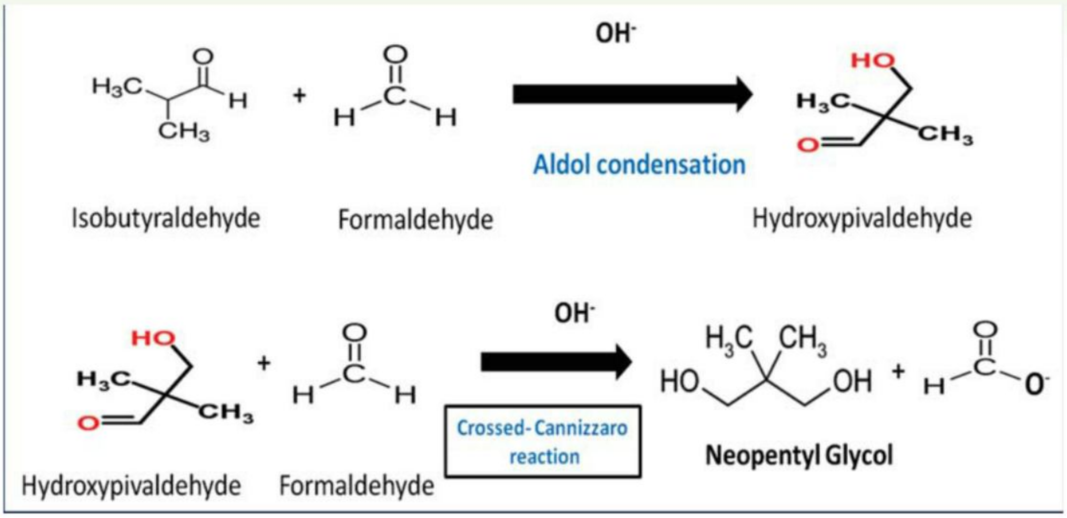


Fig 4: Reaction scheme for the synthesis of NPG through aldol condensation and crossed-Cannizzaro reaction

Production by Catalytic Hydrogenation

This process usually is performed in two stages. The type of catalysts used for the aldol addition has significant effect on the technical requirements of the hydrogenation and purification stages. Since OH- assisted aldol reaction produces significant amount of by-products, tertiary amine is being used as catalysts for the aldol addition. Hydroxypivaldehyde is formed rapidly by the reaction of isobutyraldehyde (up to 10% excess) with formaldehyde in presence of trialkyl amine as catalyst. Hydroxypivaldehyde is separated from salts by extraction with dibutylether and hydrogenated on copper chromite catalyst between 175-220 0C (Source: Ullmann's Fine Chemicals).

In a variant of this process, hydrogenation and hydrogenolysis are performed stepwise at different temperatures 120-1600C and 175-1900C. At the higher temperature, esters by products also are hydrogenated to the corresponding alcohols.

The state-of-the-art NPG plants are now use a tertiary amine catalyst in place hydroxide catalysts. Hydroxypivaldehyde is formed rapidly by the reaction of isobutyraldehyde (upto 10% excess), formaldehyde and trialkylamine (Fig.5). The complete conversion of formaldehyde occurs with a slight excess of isobutyraldehyde. The excess aldehyde is distilled with amine and the two are recycled together. The reaction is quite selective and most of the acidic by-products produced by formaldehyde reduction are absent. Hydroxypivaldehyde is separated from salts between extractions with dibutyl ether and hydrogenated with Cu, Cu/Cr, Co or Ni catalysts at 80-2000C and greater than 3.5 MPa pressure.

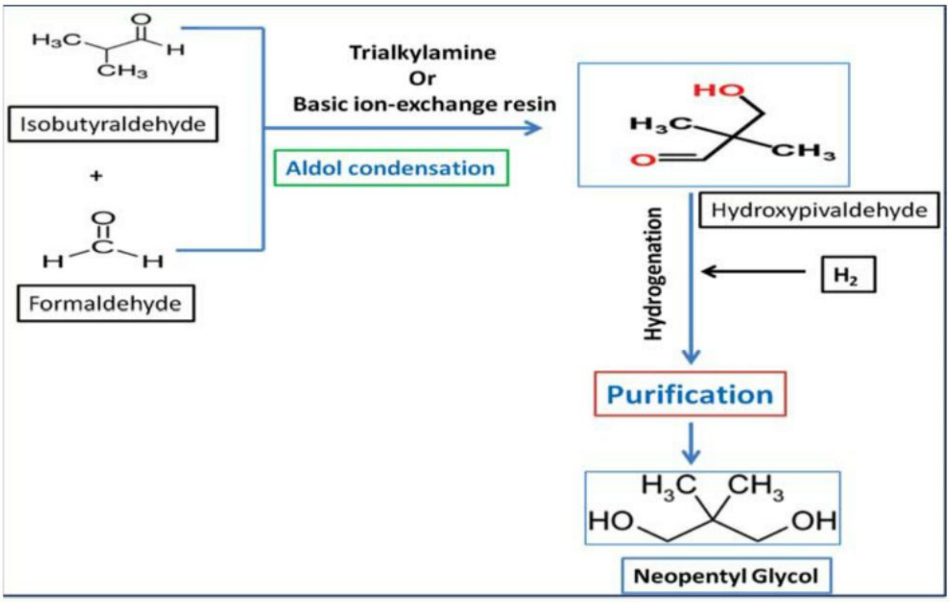


Fig 5: Reaction scheme for the synthesis of NPG through aldol condensation and catalytic hydrogenation reaction

Further advancement in the process has been achieved by using weakly basic ion-exchange resins as catalysts. Use of solid catalyst, instead of liquid catalyst, has significantly enabled easy separation of the product steams making the process even simpler. The reactions run with high selectively and therefore most of the side products which are typical of the production based on the Cannizzaro reactions, are formed only in negligible amounts (Source : Handbook of Industrial Chemistry and Biotechnology, Edited by James A Kent)

Industrial Journey of NPG productions

The first commercial production of NPG (based on process scheme of Fig 4) wasstarted by BASF in Ludwigshafen, Germany in 1959 with a capacity of below 100 metric tons per annum and was stepped up steadily. A new NPG facility with an annual capacity of 12,000 metric tons went on stream just 16 years later. This plant employed a new, environmentally more compatible BASF process that is still in use today. In order to meet the growing demand for NPG in North America as well, BASF started up another NPG plant in Freeport, Texas, in 1980, which has meanwhile been replaced with a world-scale facility. NPG demand has increased considerably in Asia, too, in recent years. BASF JCIC Neopentylglycol Co., Ltd., a 60/40 joint venture company of BASF and Jilin Chemical Industrial Co., Ltd., responded by putting into operation another NPG plant in Jilin, North East China, in 1998. As the global market leader, BASF has NPG production facilities in Ludwigshafen, Germany; Freeport, USA and Jilin, China.

Eastman invented Eastman NPG™ glycol in the 1950s, and its market share continues to grow to this day. Eastman NPG™ is available in two forms: as white, waxy platelets or molten. Slurry of 90 percent by weight with water is available and designated Eastman NPG™ 90.

Mitsubishi Gas chemical (MGC) started production of NPG at the Mizushima Plant, Japan in the year 1966. Currently, MGC produce 50,000 metric tons of NPG from this plant.

South Korea based LG Chem, started project on NPG in 1996 and within less than 3 years it started commercial product of 18000 metric tons of NPG by self-developed manufacturing process from its Yeosu Plant The capacity of this plant successively increased in 2003 to 30,000 metric tons and then in 2008 to 65,000 metric tons and then 2011 to 100,000 metric tons. At present, LG Chem is the second largest producer of NPG in the world only behind BASF. LG Chem first entered the NPG business in 1998 by becoming the world's 4th company to develop its own NPG production technology (Source: LG Chem).

Table 3: Leading Global NPG producers

Rank	Company	Locations	Capacity (1000 tonne/year)
1.	BASF	•Ludwigshafen (Germany) • Freeport, Texas, (USA) • Jilin (China)	165
2.	LG-CHEM		100
3.	EASTMAN Chemical	Yeosu, South Korea	87
4.	Perstorp	Perstorp, Sweden	50
5.	Mitsubishi Gas Chemical	Mizushima, Japan	45
6.	OXEA	Oberhausen, Germany	45
7.	BASF-YPC (A 50-50 JV of BASF and Sinopec)	Nanjing, China	40
8.	Shandong Fufeng Perstorp Chemical Co.,	Zibo, Shandong province, China	40
9.	Polioli	Vercelli, Italy	23

Very recently, BASF-YPC, JV of BASF and Sinopec JV starts neopentylglycol production at their Verbund site, BASF-YPC in Nanjing, China. The plant has annual production capacity of 40,000 metric tonnes. With this new plant, BASF-YPC are responding to growing demand for high-quality NPG especially in the Asia Pacific region, and at the same time strengthening the position as the global leading supplier of NPG (Source : BASF-YPC)

NPG scenario in India

As rising disposable income of Indian middle class in improving, the demand for consumer durable products is rising. As a result, demand for NPG is steadily growing in India. However, all of the NPG demand is met through imports and most of the NPG is imported from Sweden, South Korea and Japan.In the year 2015 around 24578 metric tonnes of NPG has been imported in India ((source: https://www.zauba.com).

Very recently, Swedish specialty chemicals group Perstorp, a leading manufacturer of polyol based products such as NPG, Pentaerythritol etc has signed a memorandum of understanding (MoU) with the Maharashtra Industrial Development Corporation (MIDC) to evaluate the opportunity to invest in a new production plant for pentaerythritol (penta) in India. The MoU was signed at the 'Make in India' event, organised by the Government of India as part of an initiative to drive investments in the country (Source:http://www.chemicals-technology.com/news).

Summary

Due to its unique properties, NPGis increasingly being used in environmentally friendly powder coatings for architectural applications, domesticappliances, transportation and automotive applications and general industrial applications.

The current NPG production process although highly optimised, the environmental footprints of NPG production can be improved ifpropylene and formaldehyde, the main feedstocks for NPG production can be produced from the renewable methanol. Propylene can be produced from methanol via the methanol to olefin (MTO) process while renewable methanol could be produced by converting syngas,derived from biomass/municipal solid waste (MSW)to methanol or through chemical recycling of CO2 into methanol (Fig 6).

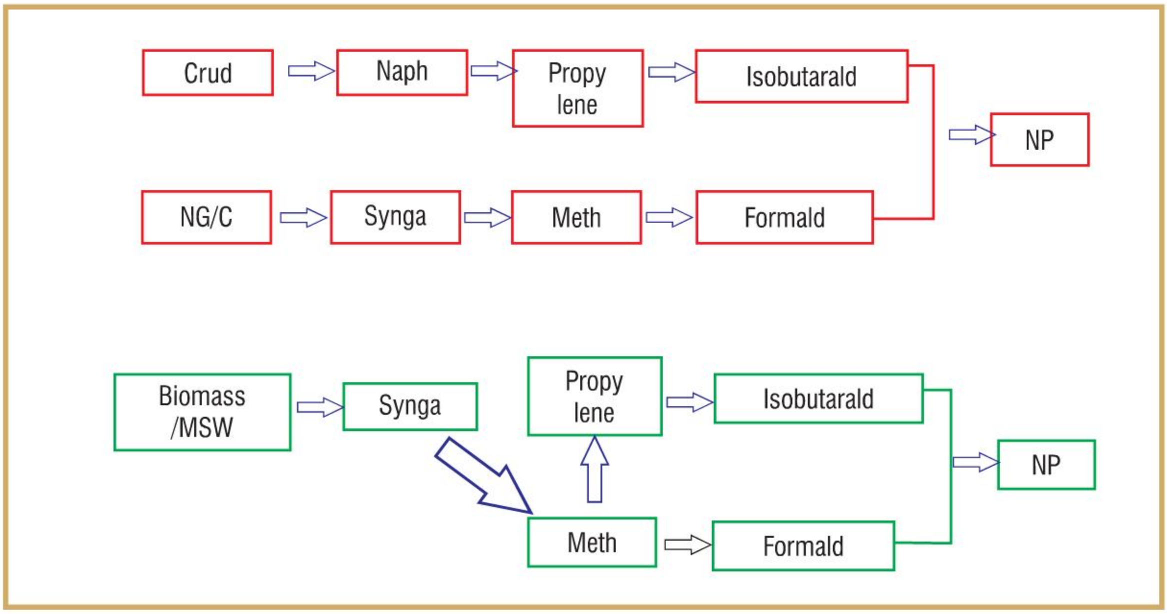


Fig 6 : Greener approach of NPG production through renewable methanol route

Further improvement in the process economics would be possible by developing more advanced dual catalyst system to make the process even simpler by conducting two reactions in a single reactor. Significant research efforts are being made in finding a suitable metal/solid base bi-functional catalyst by loading hydrogenation active metal on a solid base which would be able to catalyze the aldol-condensation of formaldehyde and isobutyraldehyde and the subsequent hydrogenation of aldol adduct in a single-reactor.

NPG will find new application particularly in the areas of like powder coatings curing at lower temperatures, thus giving good opportunities for the future. The Indian market will grow rapidly due to an increased awareness of the environmental benefits of powder coatings and VOC free paints which will drive growth for NPG.