

Catalytic Polymerisation of Gaseous Olefins to produce Gasoline

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Abstract

Among the secondary petroleum refining processes: cracking, reforming, alkylation, isomerisation, polymerization, the polymerization of gaseous olefins to yield more gasoline is the most recent discovery. This technical paper studies the method as well as the advantages of polymerizing gaseous olefins to yield more gasoline as a make-up for the gasoline produced from petroleum refining. Though yet to be incorporated into the Nigerian petroleum processing industry, catalytic polymerization of gaseous olefins to increase gasoline production could help Nigeria realise her vision of zero gas flaring by the year 2020, increase the Nigerian gross domestic product, and gross National product per capita, gross national income, purchasing power parity of Nigerians hence advancing the Nigerian economy. The raw material (gaseous olefins) is available in abundance. Products are readily marketable. For 5,000 MTPA plant capacity, total cost gave £1,672,000.00, rate of return of 33% and a payback period of 3 years. Laboratory result proved 100% product yield, and octane number of 99. Therefore a polymer gasoline plant if well managed could be economically viable in Nigeria. The plants should be located as process units of petroleum refineries and industries where gas is flared.

Keywords: Catalytic Polymerisation, Gaseous Olefins, Gasoline

1.0 Introduction

Nigeria though blessed with abundant natural resources is still rated among the third world economies. This is due to wastefulness and underutilization of these abundant natural resources. Aside minerals and Agricultural resources the most harnessed crude oil and natural gas is still wasted and underutilized due to low technology and mismanagement. Nigeria is the 12th largest producer of Petroleum in the world and also possesses the largest natural gas reserve in the continent. (Gas Exporting Countries Forum, 21st September, 2016). Nigerian National Petroleum Corporation (NNPC) says it owes the Nigerian government N 326Billion (The Punch, 17th March 2016).Corruption at NNPC has been blamed for missing funds and it is impossible to estimate how much Oil and Gas has been lost in this same manner. (The Atlantic, 18th March 2016).

In Nigeria, Crude Oil is exported for refining in the advanced countries in exchange for gasoline because of non-functional refineries hence Nigeria loses the secondary products of refining Nigerian Crude Oil. Theft and damage to Oil and Gas

facilities by Militants have led to enormous loses. Nigeria loses N13billion to oil theft and vandalism (vanguard May 31, 2016). Of the current annual gas production of about 2,000 Bscf, About 40% of the gas is being flared (Nigerian National Petroleum Corporation, 21st September 2016). Despite this enormous gas production and reserve, Nigerian power generation is now only 4,600 Mega Watts (Nigerian Electricity Regulatory commission, 21st October 2016).

To enhance higher utilization of these resources for the economic advancement of Nigeria, the Nigerian government keep setting up millennium goals and industrial revolution plans, most of which met with failure due to improper implementation. Among these industrial revolution plan is the zero gas flaring by the year 2020. Four more years, yet no technology is adopted to realise this. Substantial Nigerian national income has been lost to gas flaring. World Bank (2004) states that Nigeria is currently flaring well over 2bcf/d, probably around 2.5bcf/d and quite possibly more. This means Nigeria currently flares 75% of the gas it produces. Zero gas flaring is important as flared gases deplete the ozone layer hence increasing greenhouse effect. Among the secondary refining processes: cracking, reforming, alkylolation, isomerisation, polymerization etc. Catalytic polymerization of gaseous olefins is the most recent discovery.

This technical paper “Catalytic Polymerisation of gaseous Olefins to produce gasoline” relates more particularly to the low-pressure polymerization of normally light gases majorly olefins to form liquid products boiling in the gasoline range normally referred to as Polymer gasoline. The polymerization of these gaseous olefins to produce gasoline enhances sustainable development as gasses are not flared to deplete the atmosphere. Udofia (2000) defines sustainable development as development that meet the needs of the present without compromising the ability of future generations to meet their own needs. The polymerization of gaseous Olefins to produce gasoline could balance the Nigerian domestic fuel balance deficit to curb Nigerian peri-annual fuel shortages. Moreover, this could increase Nigerian total net exports and hence the gross national income and gross national product per capita. With this, more capital would be available to reactivate the enormous moribund technologies hence escalating the Nigerian gross domestic product, purchasing power parity of Nigerians, standard of living of Nigerians and hence eliminating poverty.

1.1 Feedstock

In most cases, the feed is light gases majorly olefins as it is difficult to purify the feed to a hundred percent purity. The feed (gaseous olefins) are cracked refinery gases which normally contain propylene and mixed butylenes, together with some propane and butanes. For special purposes purified feeds may be used, e.g. propylene or isobutylene alone. Also, Ethylene may be present in the feed.

1.2 Polymerization

Under pressure and temperature over an acidic catalyst, light unsaturated hydrocarbon molecules react and combine with each other to form larger hydrocarbon molecules. It is stated in Australian Institute of Petroleum (2013) that such process can be used to react butenes (olefin molecules with four carbon atoms) with iso-butane

(branched paraffin molecules, or isoparaffins, with four carbon atoms) to obtain substantial amount of high octane olefinic petrol blending component.

1.3 Scope of Study

This paper describes the process of polymerizing gaseous olefins to produce gasoline. The feed, catalysts, reaction mechanism, economic viability of the process and its numerous advantages are also included in the paper.

1.4 Limitation of Study

This technical paper will not go into design construction and installation of the gaseous olefin polymerisation plant even though this has been recommended because of its economic advantages.

2.0 Process Description

In the refining of petroleum oils large quantities of hydrocarbon gases are produced, e.g. by cracking processes, which contain substantial amounts of olefins. In general, the olefins are predominantly propylene and butylenes and by their controlled polymerization there may be produced higher olefins boiling in the gasoline range. Such polymers may be used as such or after hydrogenation as a high octane gasoline blending stock. The purpose of the polymerisation unit in any petroleum refinery is to couple light olefins via a cationic polymerization reaction in order to increase the production of high quality gasoline. Free radical polymerization and copolymerisation are other methods that can be applied. The feed to the unit is the C₄ cut coming from the catalytic cracker and has the approximate composition according to table 1.

Table 1: Approximate feed composition to the polymerization unit

Compound	Composition (mole %)
Iso-butane	45
Iso-butene	15
n-butene	30
Butane	10
1,3-butadien	0.07

Source: Holmberg (2012)

Small amounts of impurities like sulphur, oxygenates, nitrogen and sodium are present as well. From table 1, the percentage of Olefins in the flare gas is 45%. Besides Olefins, Paraffins may also be present in the feed (flare gas). This leads to the formation of other products like butane, propane and fuel gas. Other gaseous products majorly C₄ is recycled to the feed surge drum.

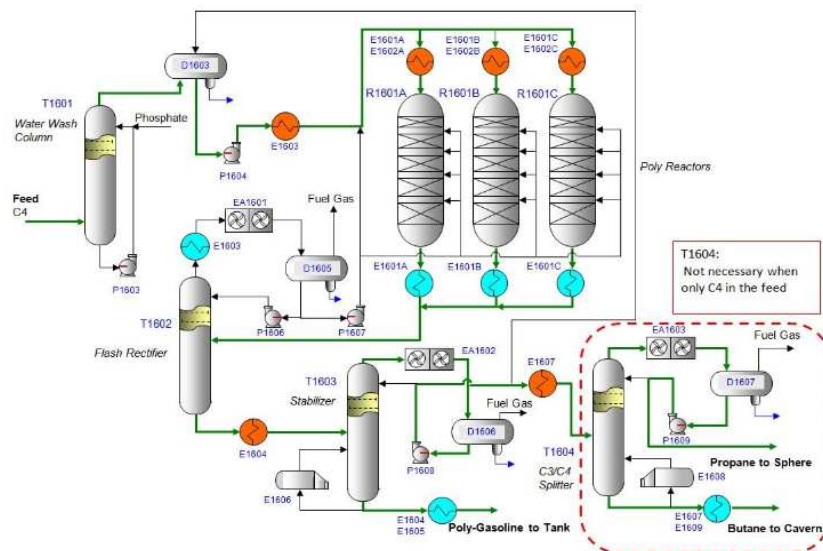


Figure 1: Process flow diagram of the polymerization unit at Preem refinery in Lysekil

Source: Holmberg (2012)

Pretreatment

The feed (gaseous olefins) enters the washing tower. Here sodium hydrogen phosphate removes alkaline components which could neutralize or deactivate the catalyst.

Separation and Dilution to 25% Concentration to avoid overreaction

Reaction: In fluidized or fixed bed catalytic reactors. For better contacting with the flare gas, the solid catalyst was fluidized. Green & Perry (1997) states that fluidization or fluidizing converts a bed of solid particles into an expanded, suspended mass that has many properties of a liquid. The olefin to be polymerized may flow upwardly or downwardly through the reactor, the liquid product being withdrawn from the bottom in either case. The catalyst liquid is much heavier than the liquid hydrocarbon product and substantially insoluble in it so that separation and recycling present no difficulties.

Cooling: Reactor products are cooled in three parallel flow heat exchangers, one for each reactor outflow.

Product Separation: In flash rectifier. An additional separation unit is necessary if this stream contains propane and butane.

Stabilization: Polygasoline C_5^+ is separated from C_4 and others.

Recycle: C4 is recycled back to the feed surge drum as feed to the wash water column. Lower olefins C₂H₄, C₃H₈ are present in trace amounts.

Storage: Polygasoline C₅⁺ is cooled and sent to storage. Propane, butane and fuel gas from the separation units are also sent to storage.

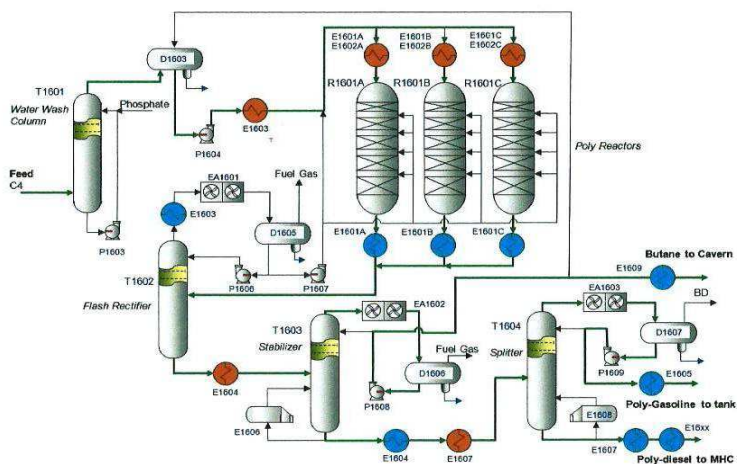


Fig. 2: Process flow diagram of a modified olefins Polymerisation plant
Source: Holmberg (2012)

A modified olefins Polymerisation unit when the feed is purely c4 is shown above. With this, polymer-diesel can be obtained as well.

2.1 Major Reactions

The major reactions in the polymerization plant of a petroleum refinery with C₄ as feed are dimerisation and trimerisation of the butene molecules i.e. formation of C₈ and C₁₂ olefins. An illustration of the reaction mechanism for dimerisation of 1-butene to a C₈ olefin is shown in figure 3. Further polymerization occurs to a minor extent and this explains the formation of heavy hydrocarbon on the catalyst that is found when it is dumped for replacement.

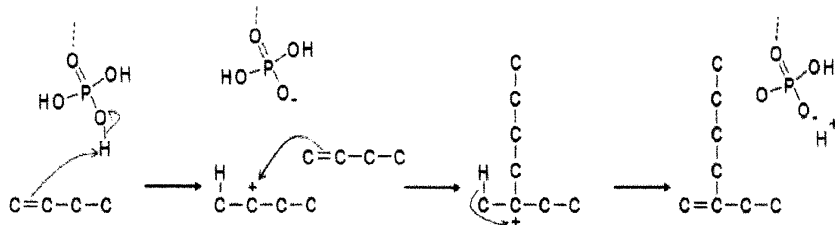


Figure 3: Reaction mechanism for dimerisation of 1-butene over Solid Phosphoric Acid (SPA) catalyst
Source: Holmberg (2012)

In figure 3, the phosphoric acid forms a free radical ($3H^+$) which is added to the butene monomer ($C=C-C-C$). The hydrogen ion attacks the reactive site (the double bond) causing the beta carbon (next to the double bond) to be deficient of electrons and hence carry a positive charge. The positive charge (C^+) keep forming a bond with another double bond so the monomer can be continuously added until the reaction is terminated at a high molecular weight (C_n) and V_i (C_n) scosity. Termination involves proton or hydrogen transfer to the phosphoric acid (PO_4^{2-}) so as to regenerate the catalyst. The polymer formed 2-ethyl hex-1-ene has improved octane number in liquid form.

If the reaction is not terminated early enough, a solid product useful for fabrication of resins and development into plastics may be formed. Continuous Viscosity measurement is therefore necessary. Decomposition of the oligomers (small monomer units, dimmers and trimers) does also occur by cracking reactions giving a continuum of hydrocarbon chains (C_2 to C_4 to C_8). However, the operating temperature is fairly low meaning that the cracking reactions only occur to a limited extent.

2.2 Reactor Scale

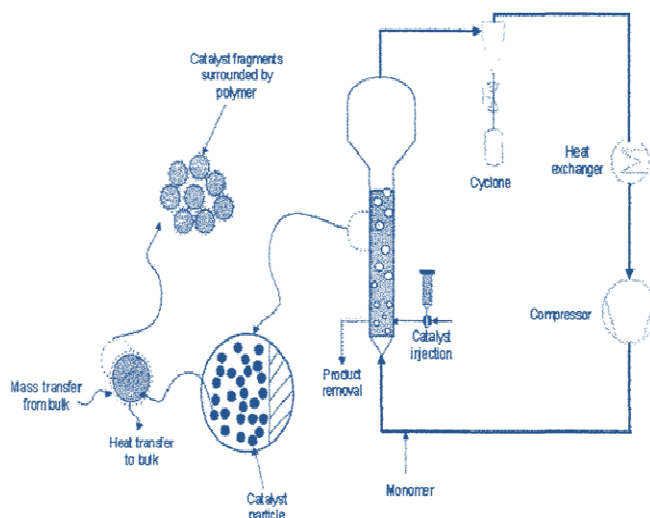


Figure 4: Several characteristic length scales in a fluid bed reactor for catalytic olefin polymerization.

Source: Holmberg (2012)

Measurement of the length in meters for each segment from the bulk to the catalyst to where the polymer reacts must be long enough to accommodate more samples for large scale production. The reactor diameter is on the order of meters, the particles are tens to hundreds of microns and the sub fragments in the order of hundreds of nanometers

Polymer properties such as the molecular weight distribution of the polymer are influenced by the type of catalyst, temperature, monomer concentration and hydrogen concentration. Temperature and concentration gradients in fluidized bed reactors are a strong function of the solids mixing and segregation rates inside the reactor, which are directly related to the reactor scale. At an industrial scale, bubble rising from the distributor plate tends to accumulate in the center of the reactor, causing an upward gulf stream of polymer powder. Depending on the hydrocarbon density, a single or more mixing cell may occur. This strong mechanism of solids mixing reduces temperature and concentration gradients in fluidised beds. In a small scale unit, axial mixing is lower and “gulf streaming” is less prominent or absent.

2.3 Components

Table 2: Components used in the polymerization reaction

Species	Function
Ziegler – Natta	Catalyst
Triethyl Aluminium	Co-catalyst
Butylene	Monomer
C ₅ ⁺ gasoline	Polymer
Hydrogen	Chain transfer agent or molecular weight control modifier

3.0 Materials and Method

3.1 Materials

Gas syringe, polymerization reactors, zeolite catalyst. Flare gas was obtained from a flare gas line of an oil and gas industry in Nigeria.

3.2 Method

Catalytic polymerization of flare gas collected from a gas flare line was carried out in the vapour phase in the presence of zeolite catalyst at low temperature and low pressure.

4.0 Kinetic Models

Kroezen (2014) gives a typical kinetic model

$$K_p = K_{p_0} * e^{(-k_d * t)}$$

$$K_p = K_{p_0} * e^{(-k_d * t)} \quad (1)$$

Odian (2004) defines the number—average degree of polymerization as chain propagation rate divided by the chain termination rate.

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{K_{pc}[M]}{K_t}$$

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{K_{pc}[M]}{K_t} \quad (2)$$

Considering that the degree of polymerization (\bar{X}_n) is also affected by other chain breaking reactions, Equation (2) can be rewritten as:

$$\bar{X}_n = \frac{K_{pc}[M]}{K_t + K_{ts} + K_{tr}M[M] + K_{trs}[S]}$$

$$\bar{X}_n = \frac{K_{pc}[M]}{K_t + K_{ts} + K_{tr}M[M] + K_{trs}[S]} \quad (3)$$

5.0 Catalyst

Table 3: Suitability of Catalyst

Catalyst	Suitability
1. Friedel craft	For polymerization of products in the lubricating oil range at high pressure. NOT suitable.
2. Halides of boron fluoride	Being gases, injecting it in the gaseous state complicates control of the reaction to give optimum yields of the desired products.
3. Dihydroxy flouboric acid $\text{HBF}_2(\text{OH})_2$	Suitable but imposes practical limitation on reaction temperature as its boiling point is 159 – 160°C
4. Ziegler – Natta	Suitable for vapour phase polymerization of olefins. Contains catalyst component in cocatalyst component.
5. Solid phosphoric acid (SPA)	Suitable. Has high selectivity towards C_8 and C_9 oligomers due to easy desorption of relatively hydrophobic C_8 and C_9 olefins from the hydrophilic catalyst surface.

6.0 Process Conditions

Temperatures: From 20°C to 30°C

Preferably, low temperatures such as room temperature or 20°C to 30°C are employed. Higher temperatures may be used at the end stages of a batch process where

the catalyst activity has begun to diminish. Temperature should be chosen to give optimum results in relation to the percent conversion, catalyst activity and catalyst stability. At higher temperatures such as those above 30°C, there is a tendency for the catalyst to evaporate unduly rapidly.

6.1 Pressure

Pressures: Sufficiently low to maintain reactant olefins in the vapour phase.

The reaction pressure is dictated largely by the source of the olefin feed and the maintenance of vapour phase operation. This, of course, means that the olefin gases are in vapour phase while the gasoline product is in the liquid phase. The process works well at atmospheric pressure but higher pressures e.g. up to 10 atmospheres or even more, may be used, especially when the olefins come from a source in which they are already under a substantial pressure, e.g. a refinery C₄ cut. In such cases there is obviously no point in reducing the pressure to atmospheric, while equally when the gasses are delivered at atmospheric pressure, there is little point in compressing them excessively. Reaction pressure should be selected with consideration that the lower the pressure, the lower will be the volumetric efficiency of the reactor and that the higher the pressure, the greater will be the investment cost of the plant.

7.0 Results and Discussion

7.1 Percent Conversion (% YIELD)

$$\begin{aligned} \% \text{ conversion} &= \frac{\text{Total gas consumed}}{\text{initial olefin content}} \times 100 \\ \% \text{ conversion} &= \frac{\text{Total gas consumed}}{\text{initial olefin content}} \times 100 \\ \% \text{ conversion} &= \frac{\text{Total gas consumed}}{\text{initial olefin content}} \times 100 \\ \% \text{ conversion} &= \frac{\text{Total gas consumed}}{\text{initial olefin content}} \times 100 \end{aligned} \quad (4)$$

The term percentage conversion as used here is a measure of the crude liquid product obtained including dissolved gas. Thus, measurement of the feed and effluent gas rates provides a measure of total gas disappearance, this gas appearing predominantly as olefin polymer, with small amounts of paraffin alkylate in some cases and as dissolved gas, in the liquid product. The gas disappearance was measured to be 100% olefin and the conversion is thus the total consumed as a percentage of the initial olefin content. This 100% is partly attributable to the presence of dissolved gas and partly to alkylation. This has been checked by measurement of the actual olefin disappearance as the difference between the olefin content of the feed and of the effluent and the results so obtained correlate reasonably well with those obtained by direct weighing of the liquid product and by measuring total gas disappearance.

$$\text{Actual olefin disappearance} = [\text{olefin content of the feed}] - [\text{olefin content of the product}]$$

7.2 Economic Viability

Octane number of gasoline = (knockmeter reading of test engine when gasoline is used) / octane
Sampson (2012)

$$= \frac{[4.05 \times 98]}{4} = 99.225\% \approx 99\%$$

An octane number of 99% shows high quality gasoline.

$$\text{Total investment} = \text{Fixed capital} + \text{working capital} \quad (7)$$

$$\text{Total cost} = \text{Total investment} + \text{operating cost} \quad (8)$$

$$£1380362.522 + £291000 = £1671362.522 \approx £167200$$

$$\approx 0.00$$

$$\text{Pay back period (PBP)} = \frac{\text{Total investment}}{\text{Average annual cashflow}} \quad (9)$$

(Coulson & Richardson, 2009)

$$= \frac{1380362.522}{454124.98} = 3.0396 \approx 3 \text{ years}$$

A pay-back period of three years is low enough.

$$\text{Rate of return on investment (ROI)} = \frac{\text{Annual net cash flow}}{\text{Total investment}} \times 100 \quad (10)$$

(Coulson & Richardson, 2009)

$$\text{ROI} = \frac{454124.98}{1380362.522} = 32.9\% \approx 33\%$$

33% rate of return is reasonable enough

For 5000 MTPA plant capacity, total cost gave £1,672,000.00. Rate of return of 33% and a payback period of 3 years. Laboratory result proved 100% product yield, and octane number of 99. Therefore, a polymer gasoline plant if well managed could be economically viable in Nigeria.

8.0 Conclusion and Recommendations

8.1 Conclusion

Catalytic polymerization of olefins in the vapour phase has been proved to be the most rewarding among all the secondary petroleum conversion processes as the raw material is gaseous olefins that should have been flared into the atmosphere to deplete the ozone layer and increase greenhouse effect. Besides enhancing sustainable

development, the Nigerian vision for zero gas flaring by the year 2020 could be realised, Nigerian net exports and gross national income will increase. High octane gasoline will be available in abundance hence balancing Nigerian domestic fuel balance deficit and eliminating Nigerian peri-annual fuel shortages. With higher capital available, the energy sector and moribund technologies would be reactivated hence escalating the Nigerian gross domestic product, purchasing power parity of Nigerians, standard of living of Nigerians and hence eliminating poverty. Feasibility study showed that the polymer gasoline plant could be very viable in Nigeria. The plant should be sited as process unit in petroleum refineries and industries where gas is flared.

8.2 Recommendations

Under the present deregulation policy and call for amendment of the Nigerian petroleum industry law, the author recommends that:

1. Catalytic polymerization of gaseous olefins be incorporated into the Nigerian petroleum industry so as to enhance the realization of government zero gas flaring vision by the year 2020.
2. It should be made legal that every petroleum refinery in Nigeria must have a polymerization plant for gaseous olefins as it is in Lysekil.
3. Other fractions from petroleum refining should be converted to value added products while catalytic polymerization of gaseous olefins be relied solely for make up for gasoline considering the abundance of these light gases in Nigeria.

9.0 Nomenclature

\bar{X}_n , Degree of polymerisation

$[M]$, M \bar{X}_n , Degree of polymerisation on $[M]$ mer concentration.

$[S]$, Chain $[S]$ transfer agent concentration.

£, Currency used in Britain

bcf/d, British Cubic feet per day

Bscf, British Standard Cubic Feet

K_{pc} , Rate constant for chain propagation

N, Currency used in Nigeria

R_p , Chain propagation rate

R_t , Chain termination rate

KP , Polymerisation rate

K_d , First order deactivation rate

K_t , K_p , Polymerisation rate constant for chain termination

K_{trM} , Rate constant for chain transfer to the monomer.

K_{trs} , Rate constant for chain transfer to the chain transfer agent.

K_{ts} , Rate constant for termination of chain transfer reaction.

$k_{p,0}$, Polymerisation rate at time = 0

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Abbreviations

ASA, Amorphous silica Alumina
FGN, Federal Government of Nigeria
GECF, Gas Exporting Countries Forum
MTPA, Metric tonnes per annum.
NERC, Nigerian Electricity Regulatory Commission
NNPC, Nigerian National Petroleum Corporation
PBP, Pay back period.
PFD, Process flow diagram.
ROI, Rate of return on investment.
SPA, Solid phosphoric acid.
TC, Total cost.
TI, Total investment.

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