

MODELING OF HYDRO-CRACKING LUMPS OF SERIES-PARALLEL COMPLEX REACTIONS IN PLUG FLOW REACTOR PLANT

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ABSTRACT

This paper presents mechanistic kinetic model of hydrocracking-lumps of series-parallel reactions of hydrocarbons fractions in reactor plant of Alesa-Elеме. The crude oil fractions kinetic parameters were determined mathematically e.g. activation energies, rate constant, and equilibrium constant of the fractions. The results obtained are presented in figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14; with the profiles depicting the actual dynamics of mole fractions of feed fractions conversion with space-time and the temperature effects in reactor 1, 2, and 3. These profiles are in agreement with typical hydrocracking process of improved products for blending into premium motor spirit in refining activities.

Keywords: Hydrocracking, kinetic model, constrain optimization, reactor, Gases C₁₋₄

INTRODUCTION

Hydro-treating and hydro-cracking processes are two major catalytic applications for refining of petroleum distillates. Hydrocracking is catalytic petroleum-refining process that cracks heavy, high boiling feedstock molecules lumped as paraffins, naphthenes and aromatics into lower boiling ones (C₁, C₂, C₃, C₄ gases) through carbon-carbon bond breaking and accompanied by simultaneous or sequential hydrogenation of unsaturates (Farrauto and Bartholomew, 1997).

Hydro-treating process is the catalytic conversion and removal of organic sulphur, nitrogen, oxygen and metals from petroleum crudes at high hydrogen pressures. Literatures have shown that hydro-treating capacity has been growing steadily since the 1970s and represents today about 50 percent of the total refining capacity (Farrauto and Bartholomew, 1997). In the development of reliable kinetic model for the hydrocracking process is an important activity from a commercial as well as a research viewpoint⁵. The design and optimization of the hydrocracking units require a detailed kinetic model that can take into account the complexity of the feed stock kinetics, while following the rules of the underlying carbenium ion chemistry⁶. Literature has shown that each fraction of distilled petroleum still contains a complex mixture of chemicals but they can be somewhat categorized. A certain sample of straight-run gasoline (light naphtha) might contain nearly 30 aliphatic, non-cyclic hydrocarbons, nearly 20 cyclo-aliphatic hydrocarbons (mainly cyclo-pentanes and cyclo-hexanes) sometimes called naphthenes, and 20 aromatic compounds (Philip, 1992), (Kolb and Kolb, 1979) and (Wittcoff, 1987).

However, the use of comprehensive process models with an accurate representation of hydro-cracking kinetics at the elementary step level can be used to reduce expensive experimentation in pilot plants. Analytically, material and energy balance was developed on the lump species of the feed depleted in the reactor plant. The principles were imperative for the modeling of hydro-cracking complex reactions of the Port Harcourt refinery reactor plant.

The process can be modeled using the concept of plug flow reactor equation to investigate the dynamics taking place in the reactor plant.

Process Concept

Literature showed that different flow-schemes have been developed for the hydrocracking process to enable various feed-stocks to be processed to yield a full range of products. The Port Harcourt refinery reactor plant which was designed by UOP consists of three-stacked continuous catalyst reforming reactors in series with re-heaters to compensate or account for the endo-thermicity of the process.

The plant/reactors are operated at the following conditions.

Catalyst bed temperature	300-450 ⁰ c
Pressure	85 – 200 bars
Liquid hourly space velocity	0.5-2.5 hr ⁻¹
H ₂ /HC ratio	3,000 – 10,000 5CFB
H ₂ consumption	1,200 – 3,500 5CFB

As a result of high hydrogen partial pressures, the use of dual functional catalysts and mobile/continuous catalyst flow to compensate for the rate of catalyst coking and deactivation being very low, thereby resulting in on-stream cycle lengths of some years. As it is expected, a typical feed-stocks used in hydrocracking process contain sulphur, nitrogen, and in-case of resid feedstock, metals which includes nickel and vanadium. Hence, these compounds have a deleterious effect on hydro-cracking catalyst. The feedstock typically requires hydro-treating prior to contacting with the hydrocracking catalyst. Hence, hydro-cracking processes are two stages involving both hydro-treating and hydrocracking reactions process. The following products yields are obtained from fractionation: light ends C₁ to C₄, light naphtha C₅-, and heavy naphtha C₆-C₈. The un-reacted or unconverted feed is recycled to the reactor so that it can be converted into commercial products.

MATERIALS

Ideally, the research borders on analytical techniques which dwell on the development of specific reaction rate equations of the first order kinetic lumps of hydrocarbon fractions resulting from the component and energy balances for the lumps. Figure1 depicts composite scheme of idealized kinetic Lumps of Hydrocracking process.

The Kinetic Lumps

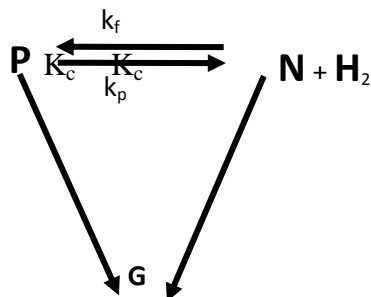


Figure1: Composite four-lump reforming reactions (Wordu, 2012), (Oboho, 2005), and (Smith, 1959), major reactions associated with the rate equations respectively.

REACTOR PROCESS MODEL

The steady state model equations components balance can be written for the kinetic species by substituting the rate laws into the plug flow reactor model equations below:

$$-\frac{dy_N}{d\tau} = K_f P_N \frac{K_{f1} P_A P_{H_2}^3 + K_{p2} P_N P_{H_2}}{K_{p1}} - \frac{K_{f2} P_p + K_3 \frac{P_N}{P_T}}{K_{p2}} \quad (1)$$

$$-\frac{dy_A}{d\tau} = \frac{K_{f1} P_A P_{H_2}^3}{K_{p1}} - K_{f1} P_N$$

(2)

$$-\frac{dy_p}{d\tau} = \frac{K_{f2} P_p}{K_{p2}} - K_{f2} P_N P_{H_2} + K_4 \frac{P_p}{P_T}$$

(3)

$$-\frac{dy_{H_2}}{d\tau} = 3 \left(\frac{K_{f1} P_A P_{H_2}^3}{K_{p1}} + K_{f1} P_N \right) + K_{f2} P_N P_{H_2} - \frac{K_{f2} P_p + K_3 \frac{P_N}{P_T}}{K_{p2}} \dots + \frac{n_c}{3} K_3 \frac{P_N}{P_T} + \frac{n_c - 3}{3} K_4 \frac{P_p}{P_T}$$

(4)

These are steady state process model of component balance for the hydro-cracking lumps with appropriate rate laws of the kinetic schemes. The rate laws for the cracking process are shown in the table 1 below:

Table 1: Rate laws for the hydrocarbons cracking process

NAPHTANENE	PARAFFINS
$-r_N \propto \frac{K_C}{P_{total}} P_{C_1}, P_{C_2}, P_{C_3}, P_{C_4}, P_{C_5}$	$-r_p \propto \frac{K_C}{P_{total}} P_{C_1}, P_{C_2}, P_{C_3}, P_{C_4}, P_{C_5}$
$-r_N \propto \frac{K_C}{P_{Tot}} P_{c1}$	$-r_p \propto \frac{K_C}{P_{Tot}} P_{c1}$
$-r_N \propto \frac{K_C}{P_{Tot}} P_{c2}$	$-r_p \propto \frac{K_C}{P_{Tot}} P_{c2}$
$-r_N \propto \frac{K_C}{P_{Tot}} P_{c3}$	$-r_p \propto \frac{K_C}{P_{Tot}} P_{c3}$
$-r_N \propto \frac{K_C}{P_{Tot}} P_{c4}$	$-r_p \propto \frac{K_C}{P_{Tot}} P_{c4}$
$-r_N \propto \frac{K_C}{P_{Tot}} P_{c5}$	$-r_p \propto \frac{K_C}{P_{Tot}} P_{c5}$

Energy Balance Model

The temperature effects along the reactor can be monitored by applying the law of conservation of energy in a differential volume element of the reactor as stated mathematically, for 1 mole of fresh feed, energy balance for a differential volume element at steady state process is as stated below:

$$N_T C_p \rho T = N_T C_p \rho (T + dT) + (\Delta H_r)(-r_i)_{1 \rightarrow 4} \rho C_p A T dz + \frac{\partial}{\partial t} (A C_p dz) \quad (5)$$

$$N_{T_0} C_p \frac{dT}{d\tau} = 3 \left(K_{f1} P_N - \frac{K_{f1} P_A P_{H_2}^3}{K_{p1}} \right) \Delta H_1 + \dots + \left(K_{f2} P_N P_{H_2} - \frac{K_{f2} P_p}{K_{p2}} \right) + \frac{n_c}{3} K_2 \frac{P_N}{P_T} \Delta H_3 + \frac{n_c - 3}{3} K_4 \frac{P_p}{P_T} \Delta H_4. \quad (6)$$

The model is analogous to the mathematical concept below:

$$\frac{dy}{dx} = f(x_o, y_o) = h f(x_o, y_o) \quad (7)$$

$$\frac{dy}{dx} = f(N_{N,o}, N_{A,o}, N_{p,o}, N_{H_2,o}, \tau_o, T_o) = h f(N_{N,o}, N_{A,o}, N_{p,o}, N_{H_2,o}, \tau_o, T) \quad (8)$$

Therefore, can be resolved simultaneously using Runge-Kutta numerically (Chapra and Raymond, 1998), (Kreyszig, 2002).

RESULTS AND DISCUSSION

Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14 depict the progressive depletion of the Hydrocarbon feeds in reactors 1, 2 and 3, as well as the temperature effects of Conversion process.

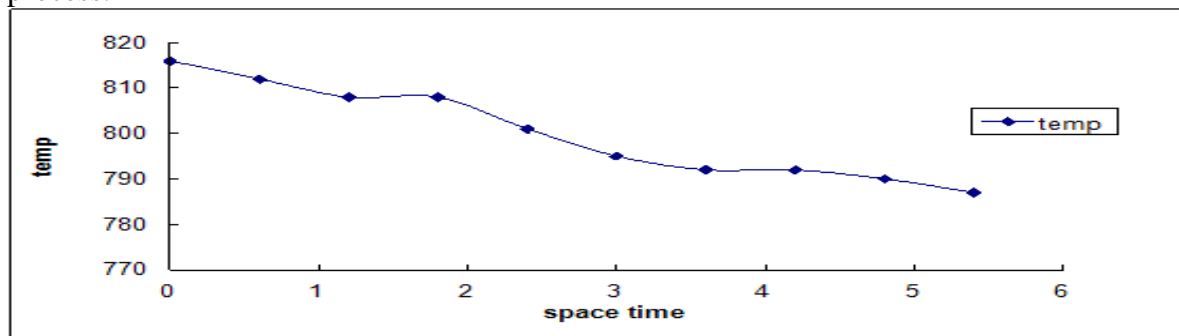


Figure1: Temperature Profile in Reactor 1

Figure 1 plot shows the temperature changes in reactor, it reduces as the reaction proceeds along the reactor tube. The drop in temperature is because of the endothermic nature the hydrocracking lumps absorb heat for cracking to take place.

Figure 2: Variations of paraffin mole fractions

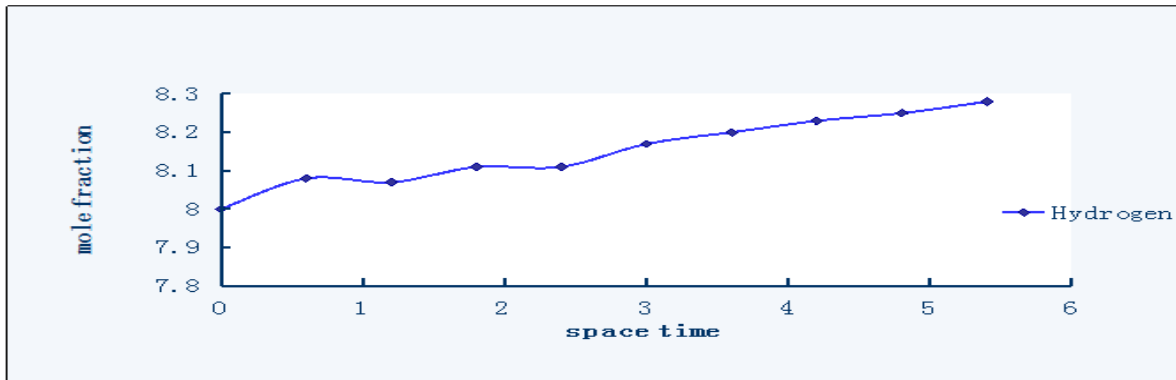


Figure 3: Variation of hydrogen mole fraction with space time

The mole fraction of hydrogen in the reactor increases with space time as the hydrocracking reaction produces hydrogen as by products which arguments hydrogen required for hydrogenation reaction in the reactor.

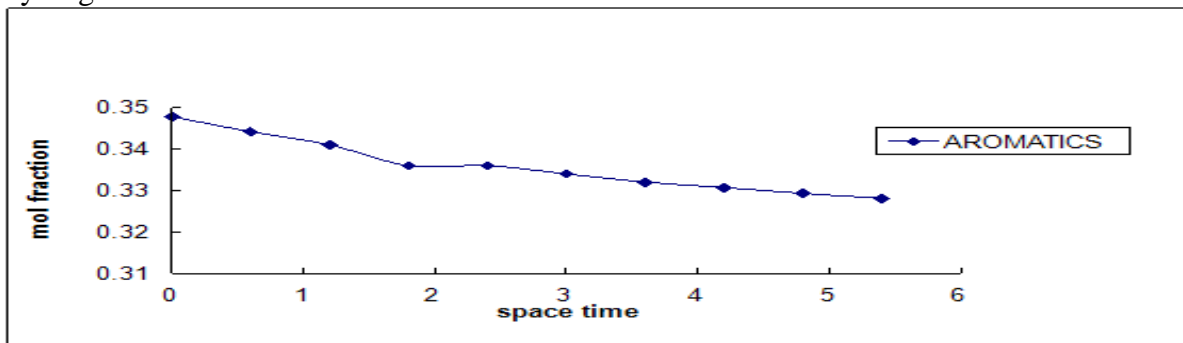


Figure 4: Variation of aromatics mole fraction.

Figure 4 Depicts that as the cracking reaction proceeds aromatics are being cracked or reduced to simpler hydrocarbons

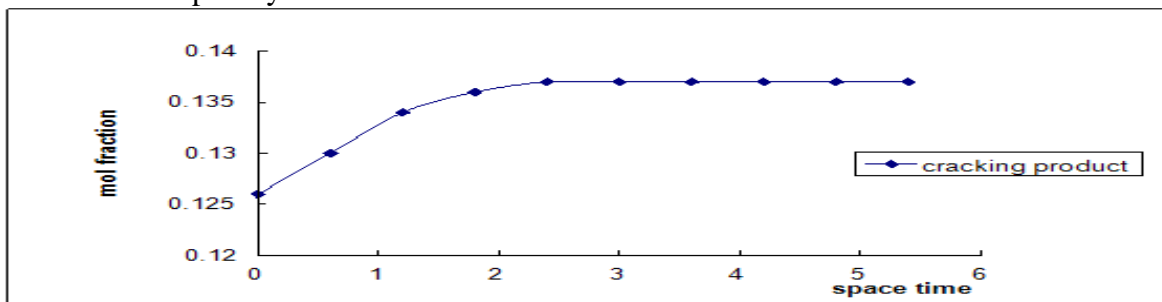


Figure 5: Cracked gases C₁, C₂, C₃, and C₄

Figure 5 shows the behavior of the cracking process with time, when the starting material was fed in, it contains high molecular weight hydrocarbons, so more products are obtained as the reaction proceeds which is the focus of the research.

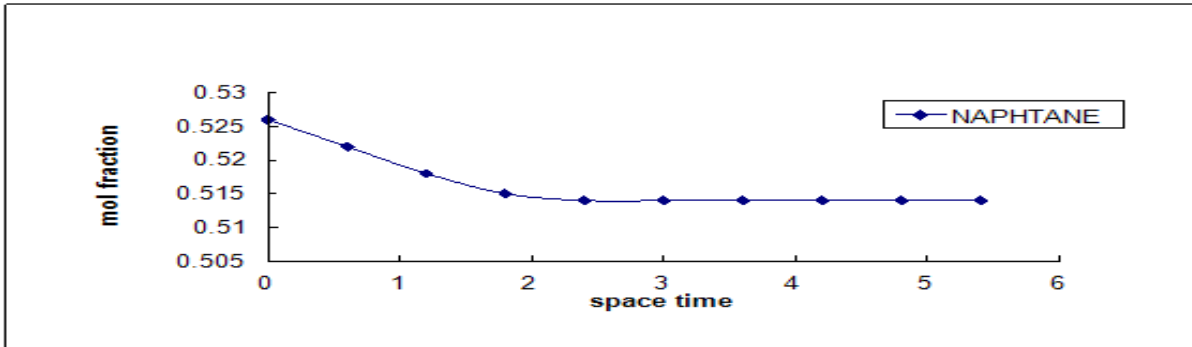


Figure 6: Plot of Naphthene against space time.

Naphthene content in the feed is high, as cracking reaction proceeds; it is cracked into hydrocarbon gases as products.

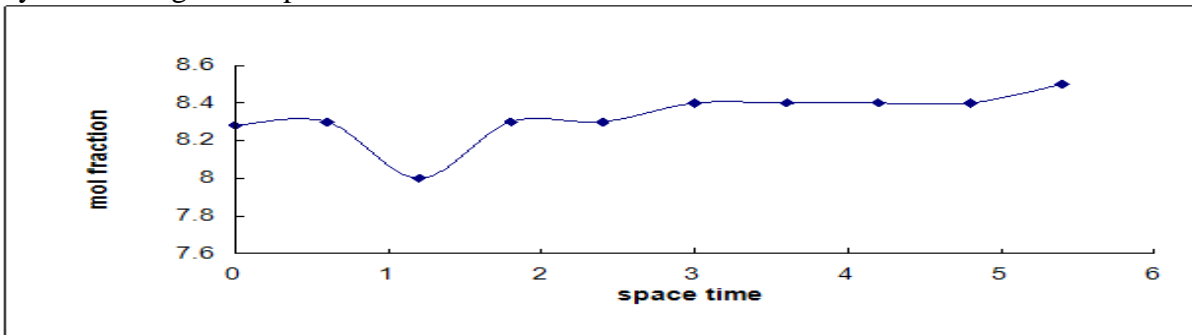


Figure 7: Variations of hydrogen mole fractions in reactor 2

As shown in reactor 1, the mole fraction of hydrogen also increases with time in reactor 2 because conversion become more faster at reactor 2.

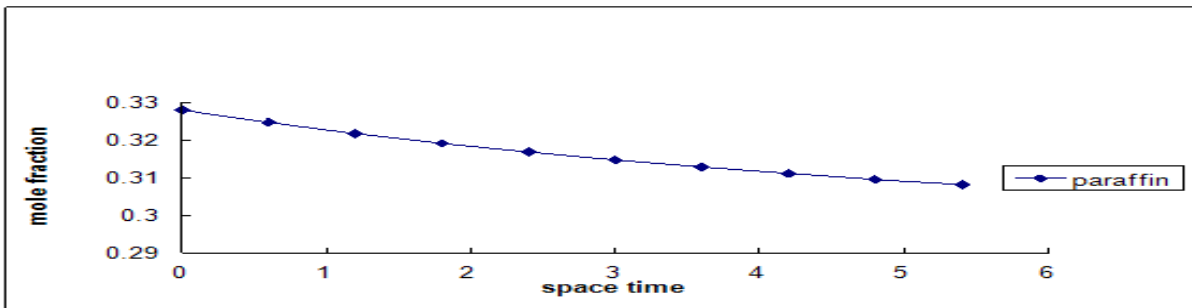


Figure 8: Variation of paraffin mole fraction in reactor 2

As evident from the plot in figure 8 paraffin mole fraction is decreasing with time as it is being consumed in the cracking to yield more gases as products.

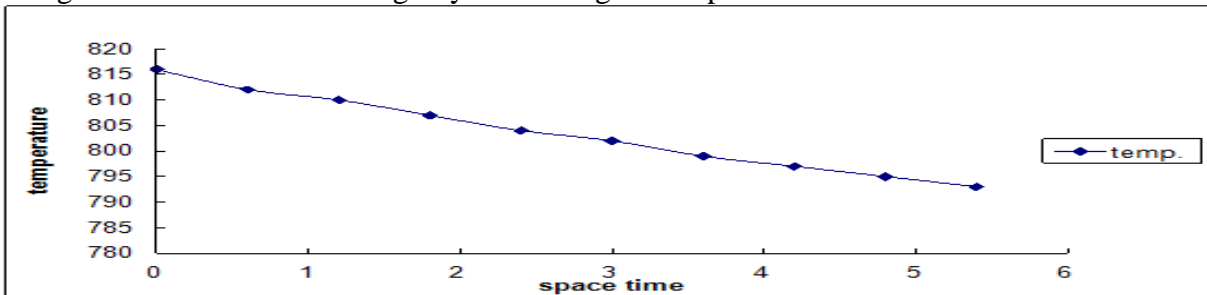


Figure 9: Temperature effects in reactor 2

Figure 9 shows that temperature in reactor reduces as the reaction proceed along the reactor; this drop in temperature is because of the endothermic nature of the reaction as the lumps absorb heat.

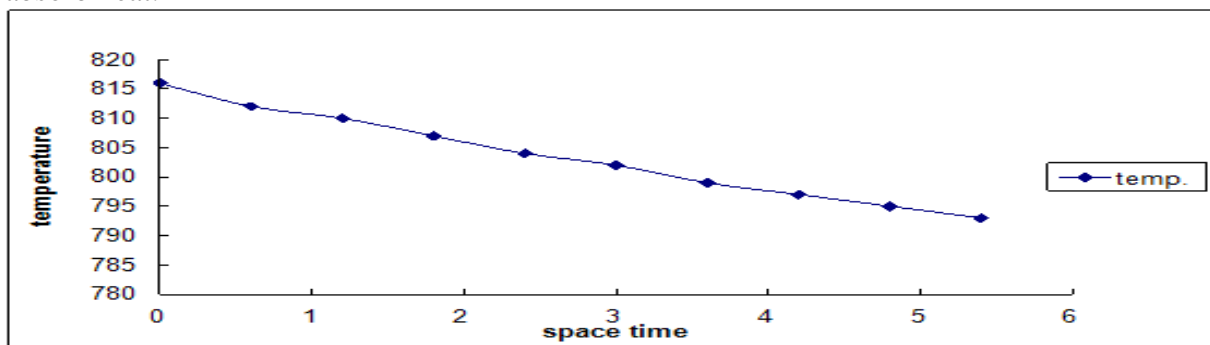


Figure 10: Temperature profile in reactor 3

Temperature progressively drops in reactor 3 due to the endothermic reactions absorbing heat and the reaction process is terminating at reactor 3.

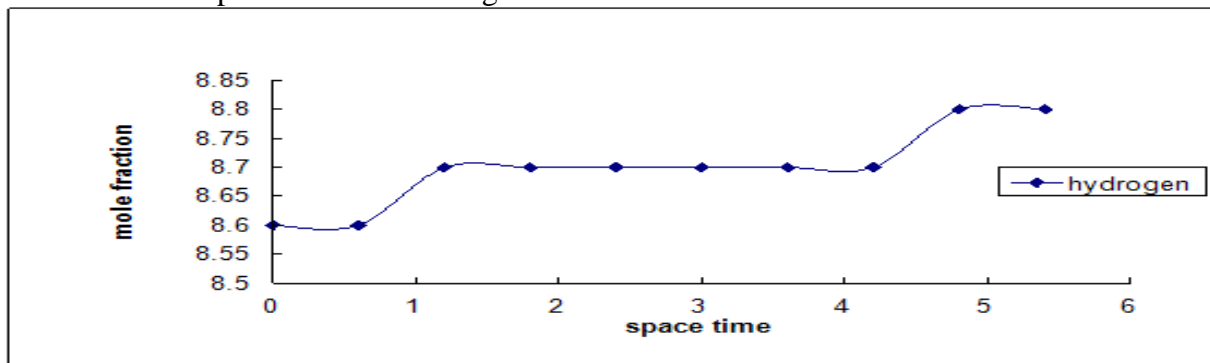


Figure 11: Variation of hydrogen mole fraction with space time.

Figure 11 shows the mole fraction of hydrogen is seen to increase up to a point; the increase is due to the fact that as the cracking reaction ends in reactor 3, also hydrogen is produced as a byproduct of the reaction. The stationary point is due to the stagnant condition of the cracking process, at those points no tangible cracking reaction takes place at the outlet of reactor 3.

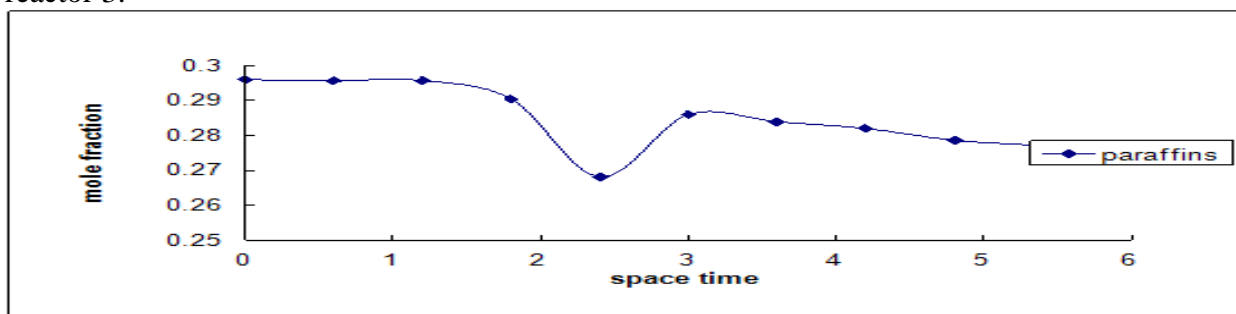


Figure 12: Variation of paraffin mole fraction with time.

Figure 12 indicates that the mole fraction decreases as expected, but a sharp- slight decrease is observed because some of the hydrocarbons undergoes dehydrogenation to yield aromatics, but as the reaction proceeds the paraffins are cracked to gases C_1 , C_2 , C_3 and C_4 .

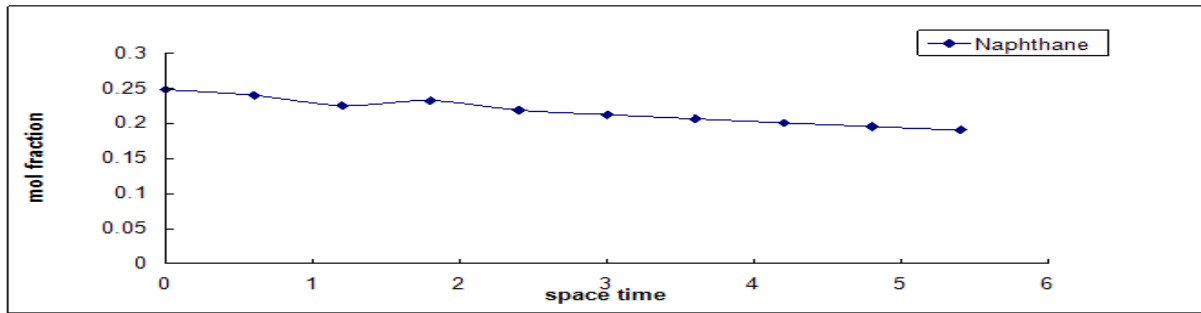


Figure 13: Variation of Naphthalene mole fraction with time.

Figure 13 also indicates that the mole fraction of naphthalene reduces; which is due to the fact that the naphthalene remaining in the mixture is cracked into gases.

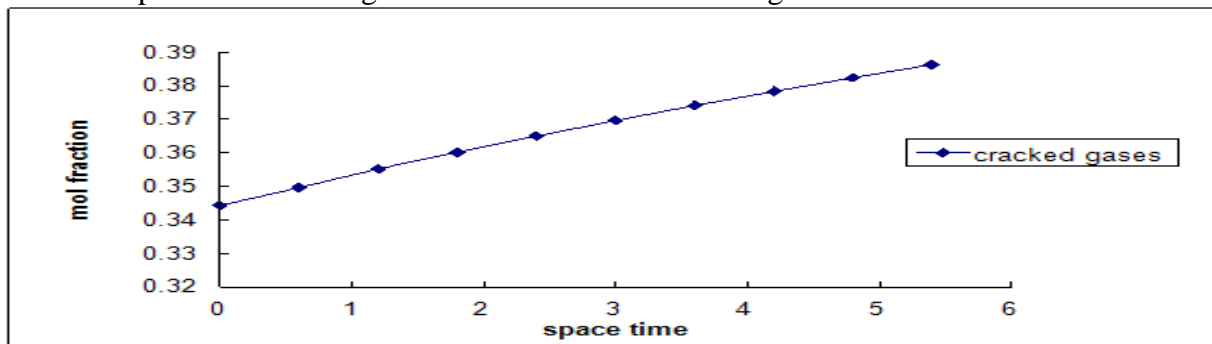


Figure 14: Variation of cracking products with time.

Figure 14 depicts that as cracking reaction ends in reactor 3, more of cracked gases C_1 , C_2 , C_3 , and C_4 is produced which is intrinsically the main objective of the research. Hydrogenation reactions are highly exothermic whereas the cracking reactions are endothermic. The amount of heat liberated in the hydrogenation reaction is greater than the heat required for the endothermic cracking reactions. The surplus heat released causes the reaction temperature to increase, thereby accelerating the reaction rate; hydrogen is injected to control the reactor temperature.

CONCLUSION

The C_1 , C_2 , C_3 , and C_4 produced is a function of the temperature and the effectiveness of the catalyst which is compensated by the continuous mobile flow of catalyst of the UOP designed reactors. The cracked gases C_1 , C_2 , C_3 , C_4 ; the propane and butane are hybridized to yield liquefied petroleum gas for domestic use. Furthermore, the C_1 and C_2 components are separated, and routed to the Nigerian liquefied natural gas plant for compression-liquefaction process; and C_2 petrochemical as feed material for furnace reactor cracking of the ethane gas to ethylene.

NOMENCLATURE

P – Paraffins, N - Naphthenes, A - Aromatics, H_2 - hydrogen,
G – Gases (C_1 , C_2 , C_3 and C_4), K_c - rate constant for hydro-cracking, K_f - rate of forward reaction, K_r - rate of reverse reaction, T-temperature, $P_{C_{1-4}}$ – Partial pressures of methane, ethane propane and butane, N_T - total number of moles of hydrocarbon species,

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