Kinetics of Catalytic Cracking of Kerosene to Ethylene on CaO-Promoted Z5 Nano-Catalyst

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Abstract

Catalytic cracking of kerosene was carried out on CaO-promoted Z5 nano-catalyst with a view to maximize ethylene yield without coke formation within a temperature range of 450±50°C, a residence time, 't of 24.2s and fluid flow velocity of 0.72m/s. The reaction formulation was based on three separate routes which were inter-related; where the overall reaction showed an overall yield of 96% olefin with a fractional conversion of ethylene at 80% and propylene 16% with no traces of coke and methane in the gas stream. Also a space velocity of $0.041s^{-1}$ was established. The presence of CaO reduced coke formation and promoted hydrogen migration from the catalyst active centre; thereby promoting reduction of hexane and heptene that are usually the primary products of kerosene cracking. Cracking at α-position on heptane was suitable for C_2 and C_3 fragmentation through route R2.

Keywords: Kerosene, Catalytic cracking, Kinetic, Fragmentation, Ethylene, Propylene, Fractional conversion.

Introduction

Cracking of kerosene through catalytic or thermal method is one major source of ethylene and propylene production in the Petrochemical industry. Many methods are used depending on product mix expected from the cracking. Major by–products beside ethlyene and propylene include butadiene, aromatic hydrocarbons and hydrogen (Adeyinka and Muganlinskii, (1994); Dishnet, 2000; McMury, 1992; Adeyinka and Otaraku, 2012). While thermal cracking operation is carried out at very high temperatures (800±100°C) with short residence time and with a low hydrocarbon partial pressure; catalytic cracking is often carried out at far lower temperatures (450±50°C) with a low partial pressure of kerosene to favour ethylene and propylene yield. Choice of catalyst and low reaction temperature is used to suppress production of propylene, aromatic and other undesirable products in the system. Many reports have used steam as cracking agent (Kellog, 1985), ultra-selective condensation was used by Stone and Webster (1985), while others used pyrolysis/quench system (Corella et al 1986).

Catalytic cracking of Kerosene uses a lower temperature 450 +50°C, operates at very low pressure between 0.66 to 1.4 atmosphere, is amenable to parameter adjustment and the process can be flexible to meet changing product demand without necessarily changing the reactor. Catalytic cracking is a flow-stream heterogeneous chemical reaction. The flow is constant in a controlled volume and obeys the kinetic flow equation often regarded as dynamic equation for homogeneous chemical reaction in a stream (Adeyinka, 1998).

$$ua=\frac{dv}{vdt}\cdot\frac{x\rho dl}{Sov\rho dl}\,\frac{dy}{vdt}\cdot\frac{x}{Sov} \qquad (1)$$

$$-r=\frac{d(uc_A)}{dl}=ua+\frac{dl_A}{dt} \qquad (2)$$

Often when the dynamic equation is substituted with a general kinetic equation where the reaction is a first-order reaction by reagent it may take the form:

$$A \xrightarrow{\qquad} A_1+A_2+---A_f \qquad (3)$$

The kinetics of equation 3 can be represented by

$$\tilde{\eta}_{oA}dx \;=K\beta_A \qquad (4)$$

Since in catalytic reaction, product formation does not inhibit the process from the onset especially when there is nearly total surface adsorption $\beta \leq 1$, with:

$$\frac{dx}{dl} = \frac{k}{\tilde{\eta}_A} \qquad (5)$$

$$k = \frac{\tilde{\eta}_A x}{l} \qquad (6)$$

The kinetic rate constant for the cracking can be established especially when a given rate of reaction is fixed for the process in a given catalytic hot bed length (Corella et al, 1986; Forissier et al, 1991; Wei and Kao, 1969). During catalytic cracking of kerosene, reactor hydrodynamics often affect adsorption phenomena, which if taken advantage of, will reduce vapour wastage, minimize ethylene/ propylene ratio with a shift to ethylene /propylene or propylene/ethylene as may be demanded.

This work reports the kinetic study of catalytic cracking of kerosene into ethylene – propylene product with an objective to eliminate the usual by-products of C_4 and aromatic hydrocarbon and coke for effective raw material production for $C_2 - C_3$ petrochemical feed stocks.

Material and Method

The reactor used in this work is a plug flow reactor. The catalyst used is a CaO-promoted nano-catalyst (Z52J), earlier reported by Adeyinka and Umesi, 2002 and Adeyinka, 1994. Kerosene of the regular market grade (NNPC- Product) was used with a flow rate of 0.65cm^3 on a total feed of 2000cm^3. The reactor was loaded with 42.6g of the catalyst and the set was heated for one hour to maintain a 450^{o}C temperature before the catalytic cracking process was carried out. Different runs were carried out within a temperature range of 500 ± 50^{o}C [450 – 550^{o}C] with a 30^{o}C variation for each run. A plunger heating system was used and the reaction products collected into a cryogenic condenser maintained at -20^{o}C. Online gas analysis was carried out to determine gas composition exiting from the reactor and initial sample analyses.

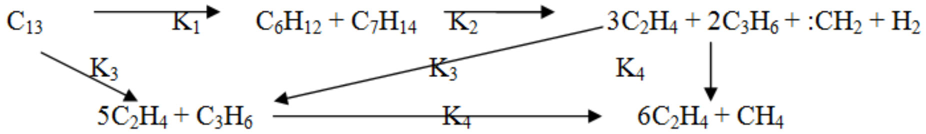
Discussion

Catalytic cracking of kerosene with an objective to produce ethylene is a selective reaction and its rate is both catalyst and temperature dependent

$$C_{13}H_{28} \xrightarrow{R1} 4C_2H_4 + C_3H_6 + C_2H_6$$
$$\xrightarrow{R2} 2C_2H_4 + 3C_3H_6 + H_2$$

Both reaction routes are common in the industry especially where a reducing promoter is not used for the catalyst. The presence of coke and acetylene which are the source of excess hydrogen gas in the reactor often reduce the yield of propylene at the expense of ethylene during the production of 1,3-butadiene which most often results in cyclic hydrocarbon during catalytic cracking reaction (Adeyinka and Muganlinsky, 1994).

$$C_3H_6 + C_2H_2 \longrightarrow C_4H_8 + C$$



Above are the suggested reaction routes for ethylene production during catalytic cracking. Since reduction of C_3 in R1 suggests coke deposition, subsequently coke deposition will reduce catalytic activity hence R2 was suggested for optimal olefin production.

If the reaction rate for catalytic cracking is assumed as:

r_{cc}= -K_1[C13H28]$\varepsilon\varphi(1-\varepsilon)$. (7)

with:

r_{cat} - rate in mols. s^{-1}m^{-3}

K_1 - kinetic constant (m$^3_{cat}$ m^{-3}catcra)s^{-1}

$[C_{13}H_{28}]$-reactant concentration M^{-3}gas
ε - void fraction
φ - deactivation function
Since plug flow reactor can be evaluated using integral method, thus

$$\frac{W}{F_{A0}} = \int_{x_{A0}}^{x_{AF}} \frac{dx_A}{-r_A} \tag{8}$$

For differential analysis

$$\frac{dx_A=}{dw/dF_A} = \frac{dx_A}{d(w/F_{A0})} = -r_A \tag{9}$$

For a reactor with varying volume and concentration:

$$\int \frac{dv}{F_{A0}} = \int \frac{dx_A}{-r_A} = V_R \tag{10}$$

Because catalytic reaction operates at near isothermal condition the pressure drop can be assumed negligible; hence feed concentration can be evaluated. At constant temperature and pressure:

$$V_R = V_o\,(+\,\varepsilon x) \tag{11}$$

From where

$$C_A = \frac{F_A}{V_R} = \frac{F_{A0}}{V_0}\left(\frac{1-X_A}{1+\varepsilon x_A}\right) = C_{A0}\left(\frac{1-X_A}{1+\varepsilon x_A}\right) \tag{12}$$

$$K = \frac{F_{A0}}{VrC_{A0}}\,(1+\varepsilon_A)\ln\left(\frac{1-\varepsilon x_A}{1-x_A}\right) \tag{13}$$

$$\frac{V_R}{F_{A0}} = \int_0^{x_{AF}} \frac{dxA}{-r_A} = \int_0^{x_{AF}} \frac{dx_A}{KC_A} \tag{14}$$

Substituting equation (12) in eq. (14)

$$\frac{V_R}{F_{A0}} = \frac{1}{KC_{A0}} \int_0^{x_{AF}} \frac{(1+\varepsilon x)}{(1-x_A)}\,dx_A \tag{15}$$

$$= \frac{1}{KC_{A0}}\left((1+\varepsilon_A)\ln\frac{1-\varepsilon x_A}{1-x_A}\right)$$

from eq. 10

$$K = \frac{F_{A0}}{V_R C_{A0}}\left((1+\varepsilon_A)\ln\frac{1-\varepsilon_A x_A}{1-x_A}\right) \tag{16}$$

From eq. (16), the rate constant for catalytic cracking at varying flow rate can be estimated and product distribution controlled. Figure 2 shows the effect of temperature on reaction rate constant.

Evaluation of Flow velocity and Fractional Conversion

From the data on the designed reactor (cross sectional area =0.78cm^2), applying continuity rule

$Q = au$

$$u = \frac{Q}{a} = \frac{0.566}{0.785}$$

Giving a linear flow velocity of 0.72cm/s, it is easy for the kerosene to totally change into vapour within a short residence time of kerosene in the hot zone before reaching the catalytic unit of the reactor.

From general kinetic equation, the fractional conversion is the amount of the kerosene that goes into reaction or is converted. This is evaluated with changes in the concentration of the kerosene at a given time using eq. (15).

$$x = 1 - \frac{CA}{C_{Ao}} \qquad 17$$

From the experimental data at 773K ($C_A = 0.00081$; $C_{Ao} = 0.004$)

$$X_A = 1 - \frac{0.00081}{0.004} = 0.80$$

Since there was no kerosene in the reaction product, a total kerosene conversion was assumed. This showed a conversion of $X_A = 0.96$. This agreed with the experimental analysis where the yield of olefin in the reactor was 94.80%. From flow analysis, the residence time for the reaction was evaluated. Also, using the principle of space time and the reaction data,

$$\tau = \frac{V_R}{V_0} \qquad 18$$

$$= \frac{13.6929}{0.5664} = 24.2s$$

The space velocity was established as $0.041s^{-1}$ which is in agreement with a fast catalytic reaction.

Evaluation of Ethylene Yield

Considering a reaction scheme that followed **R1** and **R3**. For the cracking of kerosene, the rate is assumed to be of first order in **R1**, but for the conversion of hexane – heptene the reaction is of second order with a disappearance rate for kerosene (kg species converted/kg cat) assuming a rate equation of the type

$$R_B = K_1 + K_3 C_{A0}^2 \varphi \frac{\varepsilon_R}{(1-\varepsilon_A)\rho_{subscript}} \qquad (19)$$

$$R_A = (K_2 C_{A2} - K_1 C_{A1}^2) \varphi \frac{\varepsilon_R}{(1-\varepsilon_A)\rho_s} \qquad (20)$$

Where ψ is the catalytic activity and is equal to

$$\varphi = \frac{C_K - X}{C_K} \qquad (21)$$

Equation (17) had been previously verified by the author (Adeyinka and Muganlinskii, 1994) and it can be established that in the presence of reducing promoter, catalytic cracking will promote ethylene production over hexane/heptane. From equations (17), (18) and (19), the rate of ethylene/propylene yield can be defined as:

$$-r_{con} = k_3 C_{A2}^2 + K_1 C_{A2} \frac{C_K - X}{C_K} \frac{\varepsilon_R}{(1-\varepsilon_A)\rho_s} \qquad (22)$$

From equation (22), final formations of only C_2 and C_3 olefin without coke or methane suggested that K_2 is insignificant at the operating condition, thus the effect of CaO, as a promoter, enhanced dehydrogenation over hexane – heptene fragmentation that usually proceed during thermal cracking at elevated temperatures. From kinetic evaluation, the catalytic cracking rate of 0.566m/s, with a rate constant of $6.61cm^{-2}g^{-1}s^{-1}atm^{-2/3}$ was established. This is in conformity with the result in Figure 1, where the lnK is nearly constant at varying temperatures.

R_2 pathway suggested that fragmentation of C_{13} into C_6 and C_7 (hexane and heptene) may serve as a better route. This is subject to the fact that if the methylyl radical ($:CH_2$) produced will be adsorbed onto the catalyst thereby leading to a combination reaction with another methylyl radical as in chain termination thereby leading to a dimerization reaction.

$:CH_2 + :CH_2 = C_2H_4$

This route was earlier reported for oxidative pyrolysis (Adeyinka and Muganlinskii, 1994). From bond energy point of view, this dimerization reaction is faster than hydrogenation reaction for $:CH_2$. Absence of methene and coke in the reaction product confirmed that both R_1 and R_2 are likely kinetic routes for the catalytic cracking of kerozene on the reported catalyst. Also, the near isothermal condition of the reaction suggested that contact time was very short, as indicated by the space velocity.

Conclusion

Kinetic evaluation of catalytic cracking of kerozene to produce ethylene/ propylene over a CaO-promoted Z5 nano–catalyst showed steady state behaviour where catalyst load and activity were viewed as rate-limiting parameters. Kinetic analysis showed that rate constant and extent of yield of olefin without coke and methane can serve as raw material feed for ethylene/propylene source. Also, good rate constant and yield at low temperatures can be used to predict an industrial scale-up with accurate rate evaluation and reactor modelling.

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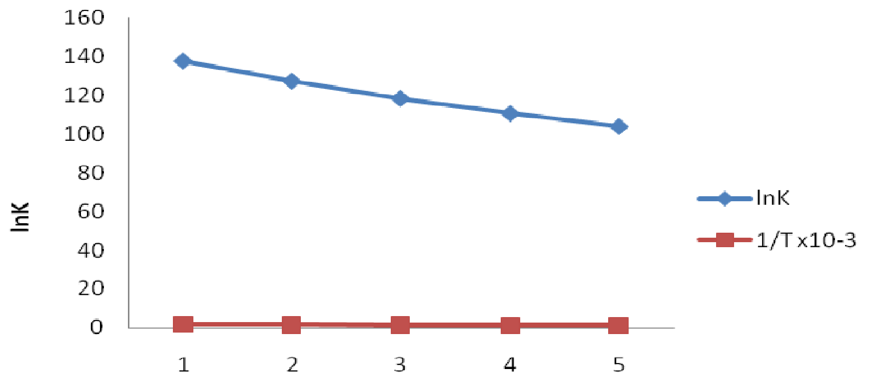

Fig.1 Effect of Temperature on Reactions Equilibrium

Nomenclature

a - cross sectional area
u - Flow velocity of reagent
V - Overall reactor volume
x_a - Yield or fractional conversion
S_{ov} - Surface area of cat (unit surface available for reacting)
ρ - density of kerosene (kg/m^3)
C_A - concentration of kerosene
C_{A0} - Initial concentration of kerosene
K - Overall reaction rate constant (S^{-1})
β - surface adsorption
l - reactor height
L - catalyst height in hot bed.
W - Mass of catalyst
F_{Ao} - Molar flow rate of kerozene
V_R - Total reactor volume
$-r_A$ - rate of kerozene conversion
Q - Volumetric flow rate
gram of cat adsorbed per gram of catalyst
R_A - Rate for monomolecular reaction
K_1 - rate constant for ethylene propylene
K_3 - rate constant for overall ethylene – propylene yield.
ρ_{cat} - density of catalyst (g/cm^3)
ε - Expansion factor
τ - space time for the reaction (s)
φ - deactivation function
$\tilde{\eta}_{0A}$ - mole number of reacting kerosene in the reactor.