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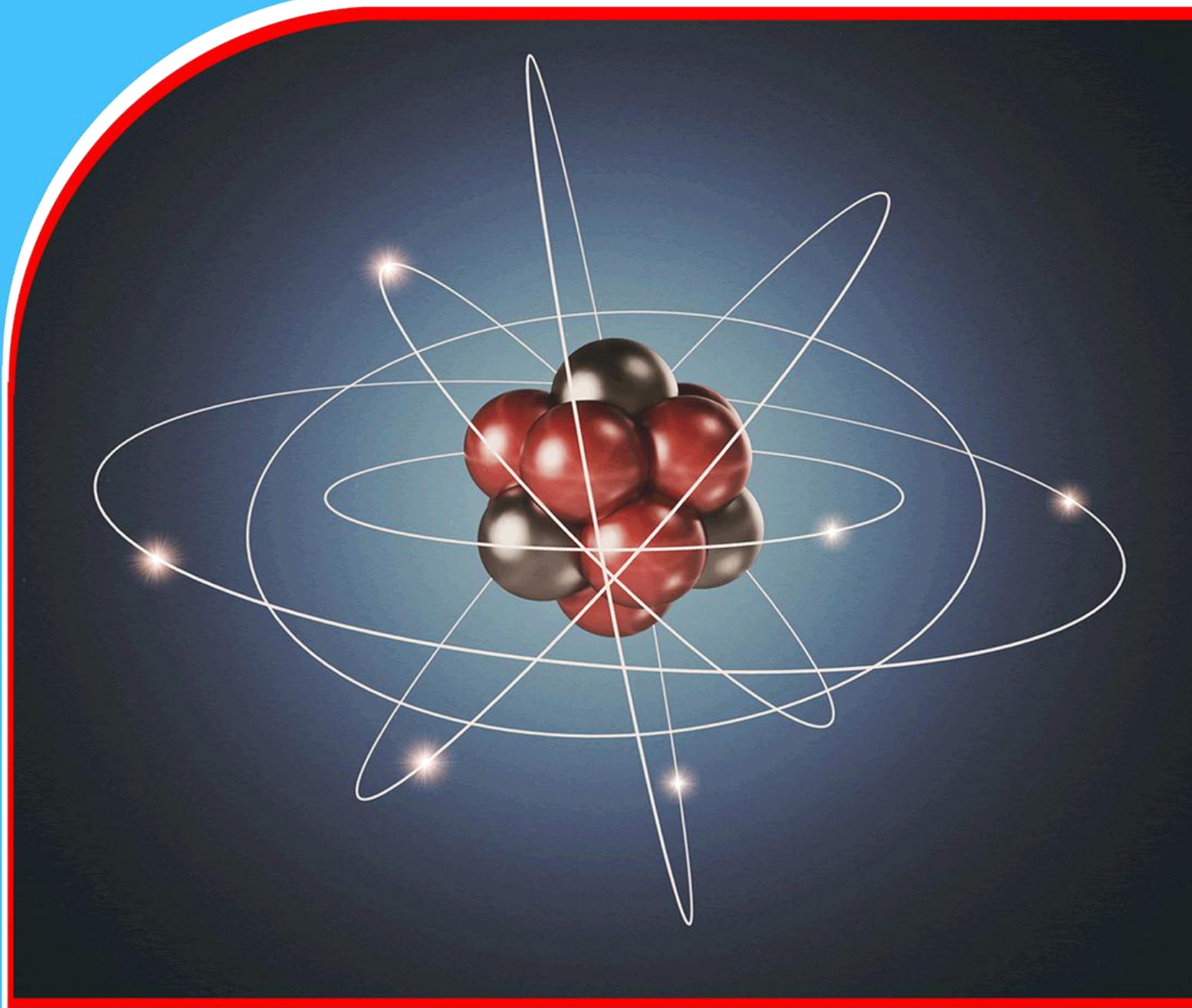

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ABSTRACT

Purpose: Objective of the work was to test efficacy of the proposed flame chemistry and collision kinetics for prediction of process parametres through determination of the effect of basic process parameters on yield (which includes but not limited to grade of carbon black produced).

Methodology: The research methodology in this work was simulation of an industrial Carbon Black Reactor based on reaction kinetics from flame chemistry which assumes that primary particle formation and particle growth is strictly by collision of molecular nuclei with gas molecule as proposed by the collision theory. Decant oil from the Fluid Catalytic Cracking Unit (FCCU) of the Warri Refinery and Petrochemical Company Limited of Nigeria represented by naphthalene was used as feedstock in the simulation while methane gas is the fuel for combustion needed to attain the reaction temperature.

Findings: Results showed an excellent quantitative prediction of trends by models. Qualitative predictions gave far higher parameter values, something easily attributable to the excessively high values of kinetic data used for model testing.

Recommendation: The simplifying assumptions of these models completely ignored microscopic phenomena such as interface mass and heat transfer and other similar processes. Consequently, the model can be improved upon by introducing some of these processes as identified.

Keywords: *Simulation, Reactor, Carbon Black, Petroleum*

1.0 Introduction

Carbon black is virtually pure elemental carbon in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions (Gardiner et al., 2001). Its physical appearance is that of a black, finely divided pellet or powder. It is essentially carbon in the form of extremely fine particles that have an amorphous molecular structure. Other than carbon, also present are very small quantities of other elements such as oxygen, hydrogen, and sulfur occurring in various functional groups bound to the carbon mass. In addition, small quantities of condensed hydrocarbons are absorbed. By varying the amount of oil and air, the internal temperature of the furnace can be altered, which permits manipulation of particle size leading to different grades of carbon black produced (Sebok and Taylor, 2001).

Two methods of carbon black production are most prominent, the world over. These are furnace black and thermal black processes with the former being the most common (Medalia et al., 1973). The furnace black process produces carbon black by blowing petroleum oil (heavy aromatic oil) or natural gas as raw material (feedstock) into high temperature gases to combust them partially as shown schematically in Figure 1. Other processes of carbon black production include channel black, lamp black, acetylene black, etc. The characteristics of carbon black produced often depend on the manufacturing process, the most commonly used method being the furnace black process (Kirk-Othmer, 1978).

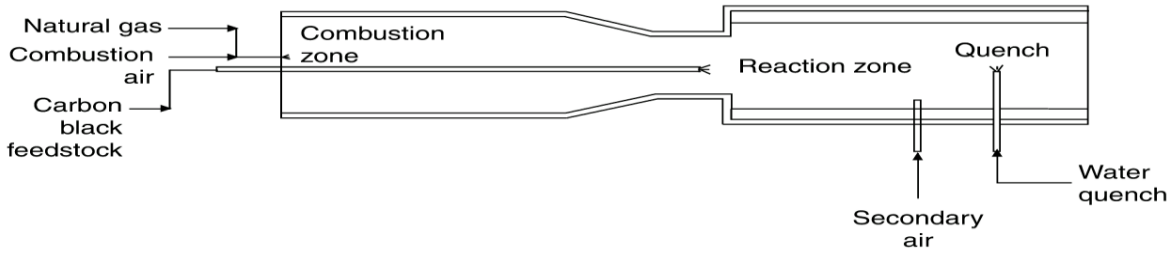

Figure 1. Carbon Black Furnace Reactor (Verlags, 1986)

Crude oil refining for recovery of elementary petroleum products such as gasoline, kerosene, diesel etc has left the industry with the problem of evacuation and disposal of the heavy refinery residue commonly referred as bottom product. Most refineries in the world especially smaller ones lack infrastructure for refining the heavy asphaltic bottom product thereby creating the problem of its effective evacuation and management (She et al., 2012). While several products such as asphalt, lubricating oil base stock (LOBS), etc are all derived from crude oil residue, decant oil from FCCU is mostly used as fuel oil. Carbon black is produced by similar high temperature combustion processes (Buyevich et al., 1993a), thereby becoming a ready product of it. There is a high demand for carbon black for applications such as production of tyres, re-enforcement of natural as well as synthetic rubbers for different uses, high performance coatings, manufacture of graphite and also in plastics manufacture to mention a few. The carbon black production process therefore solves the twin problems of refinery residue evacuation or management and production of raw materials needed for several petrochemical applications (Dhulipalli, 1990).

This study simulates a carbon black reactor of the Warri Refinery and Petrochemical Company Limited to determine the predictive efficiency of reaction kinetics by the collision theory. The work thus accomplished the following objectives;

i. Developed mathematical models to describe the carbon black production process based on kinetics from the collision theory (Witt, 1968).

ii. Studied the effect of three process parameters: reaction temperature, feedrate and residence time on yield and particle size of the black produced.

iii. The predictive accuracy of the models were then determined by comparing results with industrial data.

2.0 Reaction Stoichiometry

An exact description of carbon black formation by either gaseous or liquid feed (such as refinery decant oil) is largely unavailable and left to conjecture even though quite a lot of work has been done on it. This difficulty may not be unconnected with the swift reaction where conversion of the hydrocarbon takes place only in few seconds or milliseconds, thus extremely difficult to observe and/or even measure. However, different hypotheses have been proposed for this scheme which includes but not limited to the ionization of the hydrocarbon feed in flame as shown below (Deckens and Van Tiggelen, 1959);

$$C_{10}H_{10} + 5O_2 \rightarrow 10CHO^+ + 10e^-$$

$$10CHO^+ + \frac{5}{2}H_2O \rightarrow 5H_3O^+ + 10CO$$

$$5H_3O^+ + 5e^- \rightarrow 5H_2O + \frac{5}{2}H_2$$

A three step process of carbon formation involving carbon nucleation followed by simultaneous gas phase (agglomeration) and surface reactions (growth) is considered; the nucleation step being the most critical of them (Witt,1968).

$$10C + 5\,H_2O \rightarrow 10CO + 5H_2$$

$$10C + 10CO_2 \rightarrow 20CO$$

Nevertheless, the present work shall consider possible carbon nucleation from 'pyrolytic decomposition' of aromatic or naphthenic hydrocarbons (naphthalene) as shown below;

$$C_{10}H_{10} \rightarrow 10C + 5H_2$$

3.0 Development of Reactor Model

As a theoretical study of the carbon black production process, the work adopted kinetic model from the work of Foster and Narasimham (1965) where rate equation was given;

$$\frac{dC_{Product}}{dt} = k_1 N^{1/3} C_{Product}^{2/3} \frac{\mathrm{X_{fuel}}}{T^{1/2}} \exp\left(-\frac{E}{RT}\right) \quad (1)$$

or

$$R_{Product} = k_2(1 - X_{Product})^{2/3} \quad (2)$$

where;

$k_1 = 3.87\,X10^8$

$$k_2 = k_1 N^{1/3} C_{Feed}^{2/3} \frac{\mathrm{X_{fuel}}}{T^{1/2}} \exp\left(-\frac{E}{RT}\right)$$

To develop the models describing the carbon black formation process in this work, the following assumptions were made:

i. The carbon black formation process where a tiny nucleus is formed before growing to the appropriate particle size is similar to a gas phase reaction on a solid catalyst surface, whence this system of reaction is assumed.
ii. Gas phase reactions are compressible flow systems, thus compressible flows system is also assumed.
iii. The reactor is usually a horizontal circular tube, therefore isothermal plug flow model is assumed.
iv. Compressible flow is usually turbulent especially in high temperature and velocity system like the one under consideration. However, since the system is a tubular reactor with plug flow, a laminar flow regime is assumed.

From the assumptions above, three distinct equations define the carbon black formation reactor as given below;

3.1 Equation for diffusion on a reacting surface;

Different studies assert the formation of molecular nuclei before agglomeration and surface growth akin to the gas phase reaction on a catalyst surface. Consequently, surface growth occurs by diffusion of molecular particles to the inner core before reaction as shown in the figure 2.

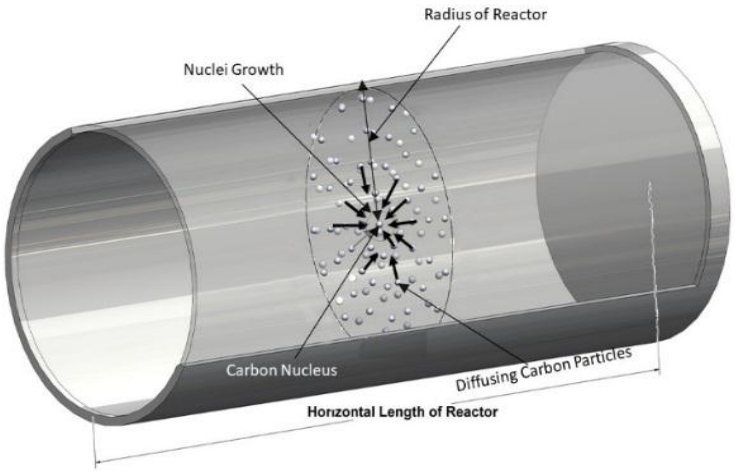

Figure 2: Nuclei Surface Growth showing Molecular Diffusion

The equation for molecular diffusion accompanied by chemical reaction in the volume element as shown in figure 2 is given by;

$$D_e \frac{d^2 C_{Product}}{dz^2} - R_{Product} dV = 0 \quad (3)$$

3.2 Equation for compressible flow;

The general continuity equation for compressible flow is given by;

$$\frac{d\rho}{\rho} + \frac{dA}{A} + \frac{dV}{V} = 0 \quad (4)$$

Rewriting (4) in terms of concentration of the reaction product gives;

$$\frac{dC_{Product}}{C_{Product}} + \frac{dA}{A} + \frac{dV}{V} = 0 \quad (5)$$

3.3 Continuity equation for plug flow reactor;

Continuity equation for plug flow reactor is given by;

$$\frac{dC_{Product}}{dt} - R_{Product} \frac{dV}{\vartheta_{Feed}} = 0 \quad (6)$$

Dimensionless Numbers:

For ease of computation of the resulting equations, the following dimensionless entities are defined;

$$X_{Product} = \frac{C_{Feed} - C_{Product}}{C_{Feed}} \qquad \sigma = \frac{k_3 R^2}{D_e} \qquad \varepsilon = k_3 t_{ref}$$

$$\emptyset_r = \frac{r}{R} \quad ; \quad \emptyset_z = \frac{z}{Z} \quad ; \quad t = \frac{\tau}{t_{ref}}$$

Substitution of dimensionless groups into (3), (5) and (6) yields;

$$\frac{d^2 X_{Product}}{d\emptyset_r{}^2} - \sigma(1 - X_{Product})^{2/3} = 0 \quad (7)$$

$$\frac{\partial X_{Product}}{d\emptyset_z} + (1 - X_{Product}) = 0 \quad (8)$$

$$\frac{dX_{Product}}{d\tau} + \varepsilon(1 - X_{Product})^{2/3} = 0 \quad (9)$$

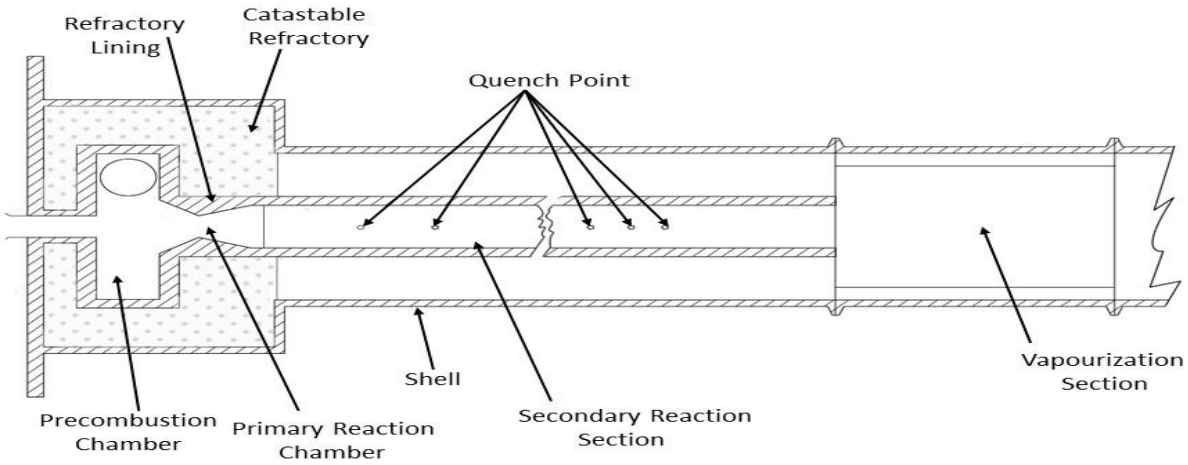

Figure 3: Schematic of WRPC Carbon Black Reactor (WRPC Operational manual)

Initial and Boundary Conditions;

To appropriately define boundary conditions for carbon black formation, reference is yet made to the reaction of a gas – solid system. In this system, it is assumed that concentration is maximum at the surface of the particle whence the maximum particle radius. Also, reaction effectively starts after particle nucleus has been formed, thus giving a finite value for radius when time ($t = 0$). However, to maintain symmetry of the particle in diffusive flux (Richardson, vol. 3), the particle radius is assumed to be zero at the start of reaction as given below.

$$t = 0 \;\; ; \quad r = 0 \;\; ; \quad \emptyset_r = 0 \;\; ; \quad z = 0 \;\; ; \quad \emptyset_z = 0 \;\; ; \quad \frac{\partial X_{Product}}{d\emptyset_r} = 0$$

$$t = t_{Max} \;\; ; \quad r = R \;\; ; \quad \emptyset_r \neq 1 \;\; ; \quad z = Z \;\; ; \quad \emptyset_z = 1$$

4.0 Results and Discussion

Simulation of carbon black reactor in this work using a hybrid of diffusive flux in tubular reactor model was based on two performance variables: product yield and size of carbon black particles. Product yield was analysed as fractional conversion of the feed while particle size was based on the number of carbon black particles per unit volume. Size is a critical element in the production of carbon black, as it determines the grade and therefore the market value of the product (Dannenberg et al., 1992). Performance evaluation of models were carried out by computations using process parametres of a carbon black reactor from the Warri Refining and Petrochemical Company Limited shown in Table 1 and kinetic data from the work of Witt (1968) shown in Table 2.

The overall rate constant k3 was evaluated based on k1 which is the rate constant of the primary reaction, and the particle density. These two kinetic parameter which are the main rate determining factors both showed increase on the overall rate constant as represented in Figure

4. However, even with a magnification of 10^4 of k1, effect of Nparticle is more severe on the overall rate constant.

Table 1

Process Data from WRPC

S/N	Variable	Value		Variable	Value
A.	**Feed Parametres**		D	**Reactor Parametres**	
1.	$C_{Feed}(kg/m^3)$	1000.0	1.	$P_{Reactor}\ (kg/m^2)$	5500 - 6800
2.	$\vartheta_{Feed}\ (m^3/s)$	3.3E-04 - 3.61E-04	2.	$d\ [N330](m)$	3.3 E -9 – 2.3 E -8
3.	$P_{Feed}\ (kg/m^2)$	2.34E5	3.	ρ(kg/m^3)	1.8E03
4.	$C_{PFeed}\ (kg/m^2)$	473.15 – 523.15	4.	$Yield\ (\%)$	85 - 95
	$C_{PFeed}(J/kgK)$	1720	5.	$T_{Reactor}$(K)	1573.4 - 1773.4
B.	**Air Parametres**		6.	$\tau_{Reactor}\ (s)$	0.001 – 0.004
1.	$\vartheta_{Air}\ (m^3/s)$	0.834 - 0.889	E	**Reactor Dimensions**	
2.	$P_{Air}\ (kg/m^2)$	5500 - 6800		Length (Pre-C, m)	3.0
3.	T_{Air}(K)	743.4 - 823.4		Diametre (Pre-C, m)	1.0
C.	**Fuel Parametres**			Length (Prm-R, m)	1.6
1.	$\vartheta_{Fuel}(m^3/s)$	0.042 - 0.047		Diametre(Prm-R, m)	0.4 – 20
2.	$P_{Fuel}\ (kg/m^2)$	4.E04		Length (Sec-R, m)	4.4
3.	T_{Fuel}(K)	298.4		Diametre (Sec-C, m)	0.38

Source: Adapted from WRPC Process Manuel

Table 2

Kinetic Data for Computations

S/N	Parametre	Value
1.	$Rate\ Const., k_1\ (1/sec)$	3.87 $E8$
2.	$Rxn\ Rate;\ R_P\ (kg/m^3 sec)$	1.86
3.	$N\ (particles/m^3)$	6.58 $E21$
4.	ΔH(kJ/mol)	$-74.9\ E4$
5.	$E_A(---)$	50.1
6.	X_{Fuel}	0.00998
7.	$X_{Fuel}(2900F)$	$2.31\ X\ 10^{-4}T^{0.5}$
8.	$D_e\ (m^2/s)$	$10^{-6} - 10^{-5}$
9.	$C_p(--)$	38.05

Culled from: Witts (1968)

4.1 Effect of process Conditions on Product Yield

The effect of process conditions on product yield is given in Figures 5. Higher temperatures favour yield as there is exponential rise in yield with temperature. This is explained by the fact

that carbon black production involves cracking of long chain hydrocarbons which require high temperatures often provided by combustion chambers similar to furnaces. Generally, the gas phase combustion reaction is initiated at high temperatures and disallowed

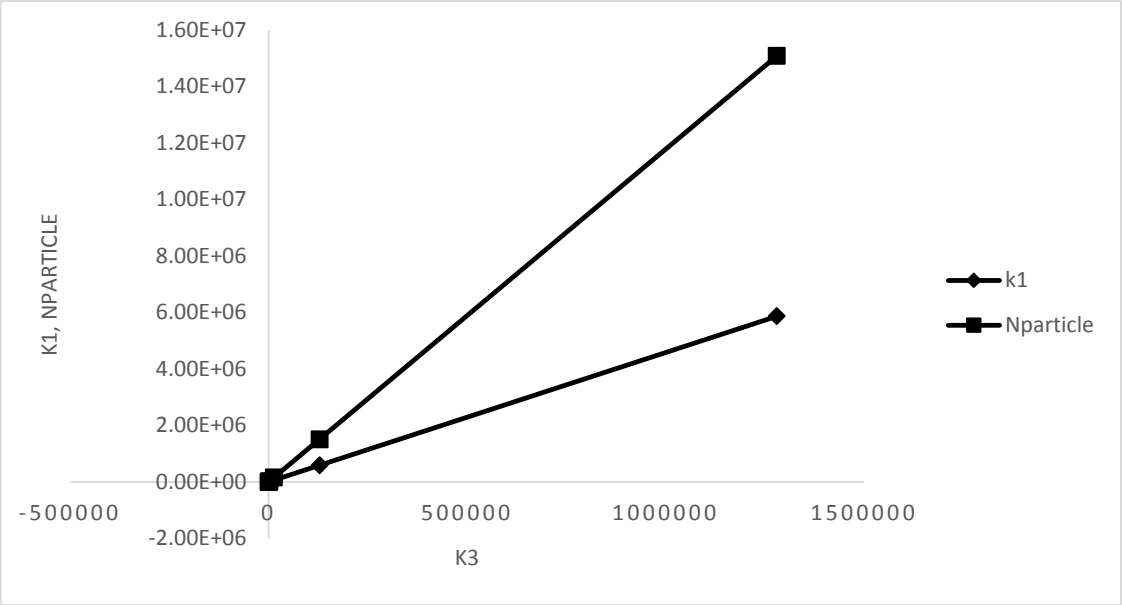

Figure 4: Effect of Particle Density and Primary Rate constant on Overall rate Constant

to go into completion by abrupt quenching, otherwise there will be formation of carbon dioxide instead of elemental carbon and carbon monoxide the desired product (Girach et al., 2014). Noteworthy however, is the quantitative prediction of temperature by the models which about three times higher than the industrial value. This may be due to the excessively large numerical factors of k1 and Nparticle used for the computations.

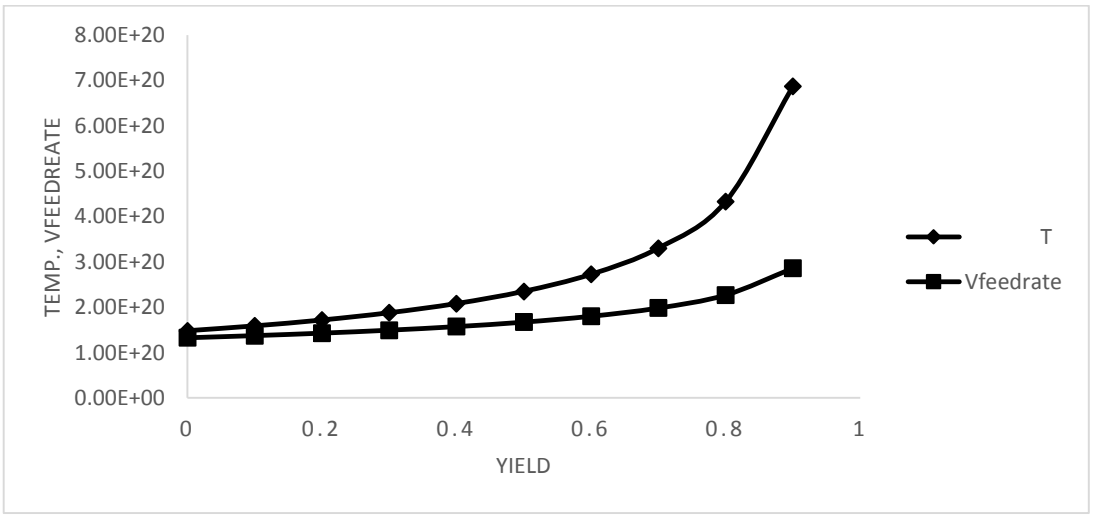

Figure 5: Effect of Temperature and Feedrate on Yield

Feedrate affects product yield in a similar pattern though in much milder dimension. Even with a magnification of (x 10^8), federate gave only a mild slope as shown in the Figure. Effect of fuel conversion and residence time in reactor on yield showed rather opposite profiles to those of Figure 5. Yield reduces with increase in these two parametres shown in Figure 6. Nonetheless, fuel conversion has more severe impact on yield than the residence time. Carbon black production is a transient reaction (Baum and Rehm, 1991) which is abruptly stopped by quenching, otherwise the reaction proceeed and gives carbondioxide instead of the monoxide. Thus the longer is the reaction time, the lower is the yield.

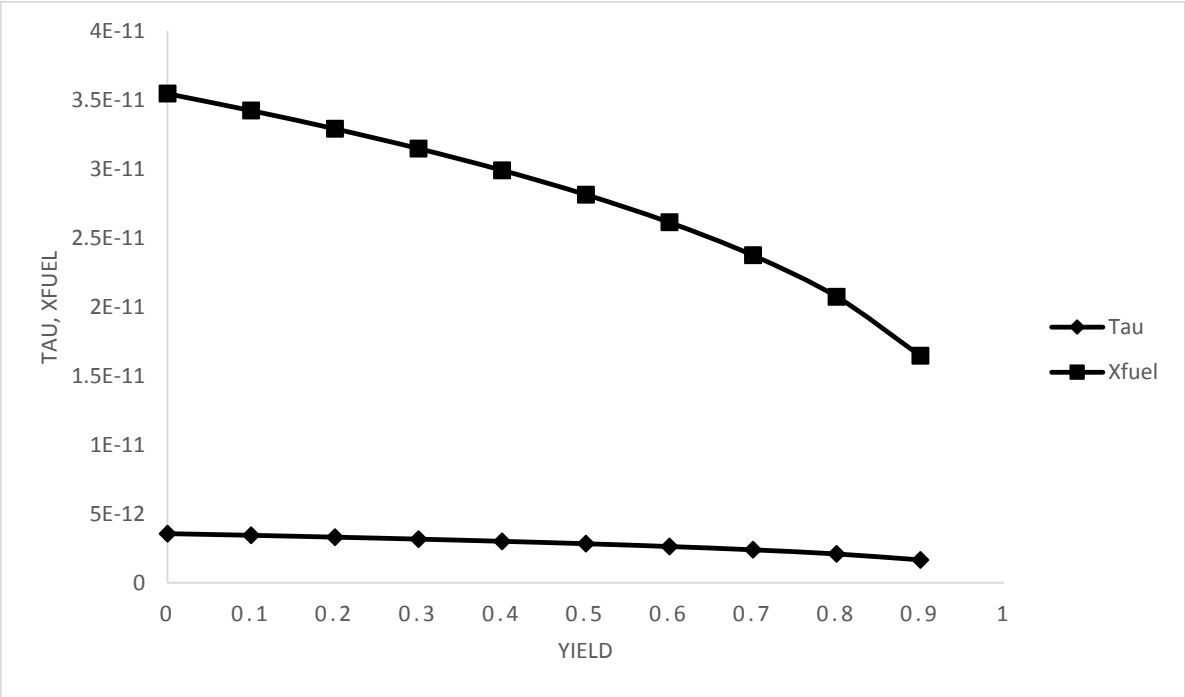

Figure 6: Effect of Residence Time and Fuel Conversion on Yield

Also, fuel conversion follows a similar pattern of behaviour. From collision kinetics, only a molecular nucleus is required for surface aggregation to take place by collision with feed molecule. A higher conversion of fuel thereby results in delayed formation of molecular nucleus for effective commencement of reaction, and lower yield. The effect of reactor length and particle radius was also determined as shown in Figure 7. Yield increases with molecular radius but reduces with reactor length. These observations are supported by need for presence of molecular nuclei for reaction and also transience of process respectively.

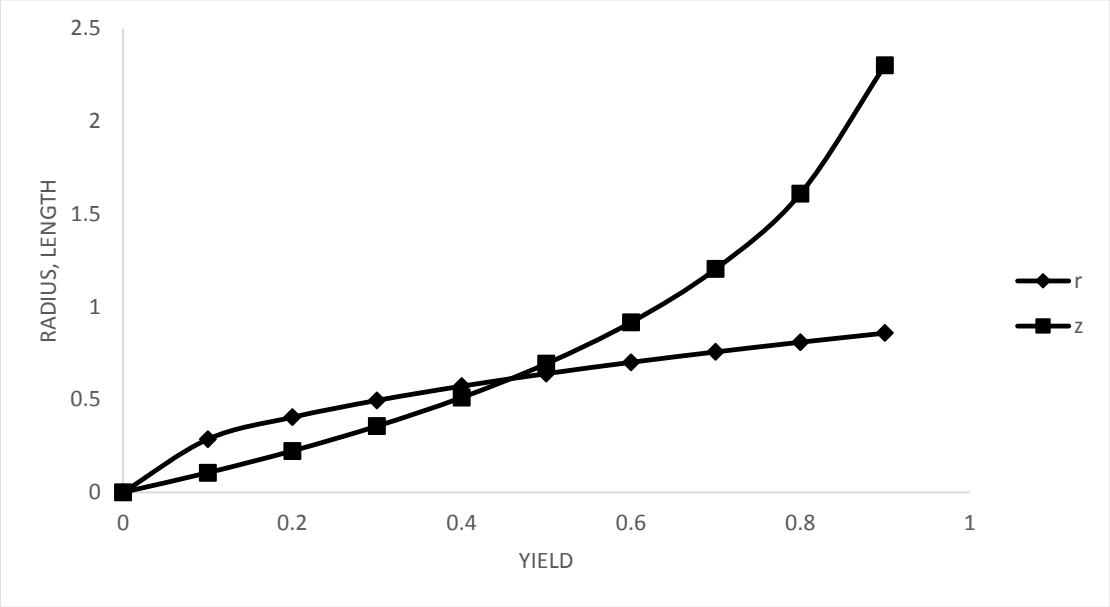

Figure 7: Effect of Particle Radius and Reactor Length on Yield

4.2 Effect of Process Conditions on Particle Size

The grade of carbon black is determined by the particle size of the black usually given by different physical parameters, viz: particle diameter, particle surface area, particle mean geometric area, particle density (or number of particles) etc. Some common market grades of carbon black based on the above parameters are N220, N330, N660, N990 etc and determines the kind of application of the grade and hence its cost. Figures 8 and 9 show the effect of process parameters on particle size. Both process temperature and federate vary linearly with particle density shown in Figure 4.

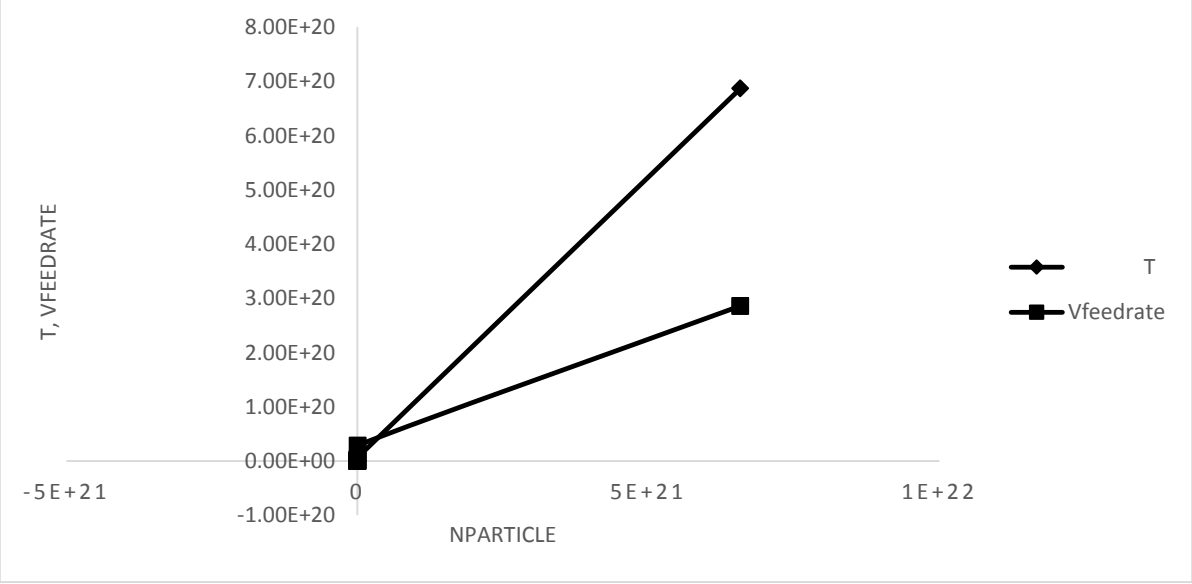

Figure 8: Effect of Temperature and Feedrate on Particle Density

Like the effect of these parametres on yield, temperature gives greater impact than federate. In the contrary, fuel conversion and residence time gave no significant impact in particle density.

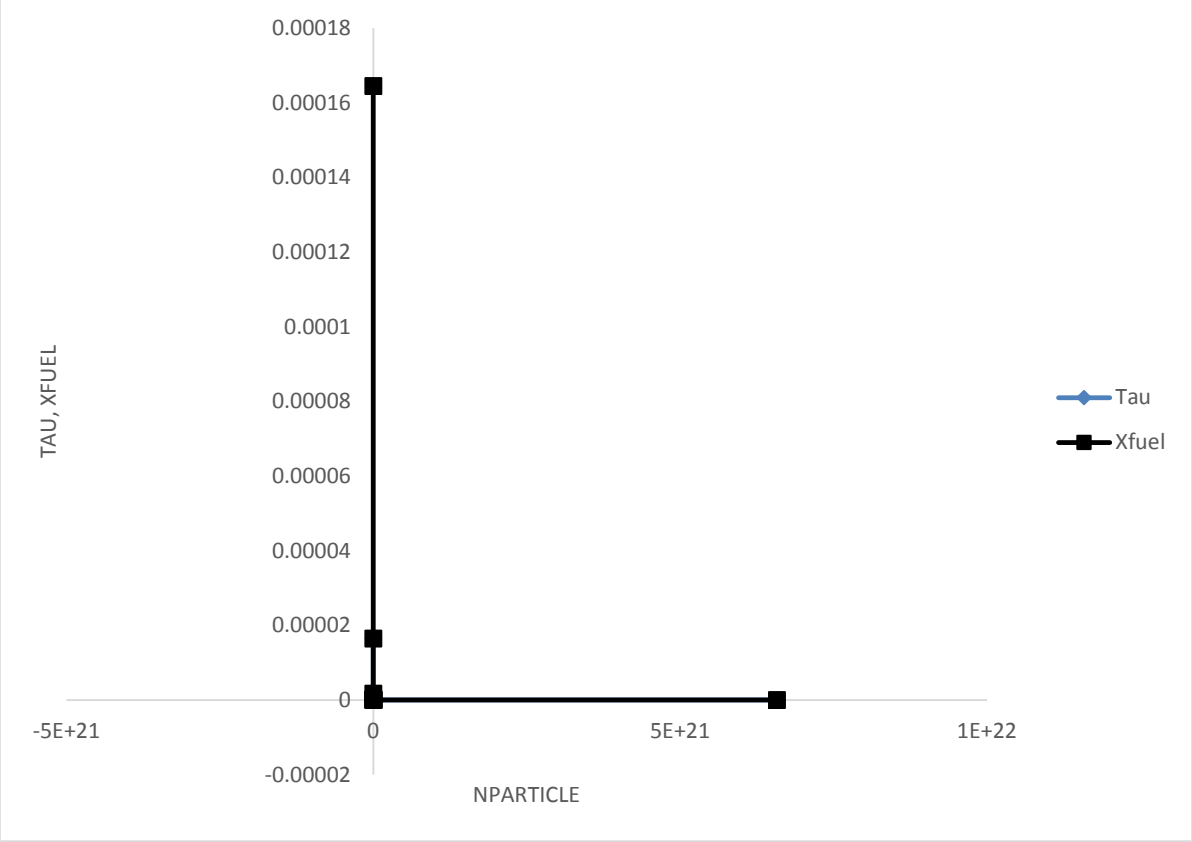

Figure 9: Effect of Residence Time and Fuel Conversion on Particle Density

This is explained by the computational data which were absolutely small factors compared to the particle density. Suffice to note therefore that the two major process parameters that can be used to manipulate the size of carbon black particles from this work are the reaction temperature and volumetric feedrate.

5. Conclusion

Predictive accuracy of the models in this work is only justified quantitatively. The effects of operating parametres on performance variable followed standard principles and theories. However, qualitative accuracy of predictions could not be verified upon. This is obviously due to the kinetic factors especially of the primary rate constant k_1 and particle density, Nparticles used for these computations. Nevertheless, the models were able to prove the applicability of the collision kinetics proposed for quantitative modelling of carbon black reactor as clearly shown.

6. Recommendation

The simplified model for predicting performance of Carbon black reactor presented in this work conforms with established principles of science, whence is dependable for application. It gives new insight such as the effect of the particle density of Carbon black as a major determinant of process parametres, being a direct consequence of the collision theory. The foregoing is the major contribution to knowledge by this work. However, it is important to note that the model was based on assumptions that oversimplified the process. Microscopic phenomena such as interface mass and heat transfer and other similar processes were ignored. Consequently, the model can be improved upon by introducing some of these processes as identified. Also, a necessary recommendation shall be the qualitative validation of the model by appropriate experimental design.

NOMENCLATURE

$C_{Product}$ = Concentration of Carbon Black (Soot)

N = Number of Particles of Carbon Black

X_{fuel} = Mole fraction of fuel (CH_4)

C_{Feed} = Molar concentration of feed (as Benzene , kgm^{-3})

τ = Reactor Residence time (seconds)

$V_{Reactor}$ = Reactor Volume (m^3)

ϑ_{Feed} = Volumetric flowrate of feed (m^3s^{-1})

z = $Length\ of\ Reactor$ (from z = 0 to L) (m)

u = $Velocity\ in$ Reactor (m/s)

D_L = Dispersion coefficient in the longitudinal direction (m^2/s)

S = Surface Area (m^2/g)

ρ = Density of Carbon Black (g/cm^2)

S_g = Geometric Surface Area (m^2/g)

d = Particle Diameter (m)

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