Process Simulation

- Proximate and ultimate analysis used
- Aspen plus process simulation software used
- Gibbs free energy minimization approach

Fischer-Tropsch Chemistry

Similar to many other Polymer reactions:

Monomer formation: $CO- + 2H_2 \Rightarrow CH_2 + H_2O$

Polymerization $CH_2- + C_nH_{2n} \Rightarrow C_{n+1} H_{2n+2}$

Termination $C_nH_{2n} - + H_2 \Rightarrow C_n H_{2n+2}$

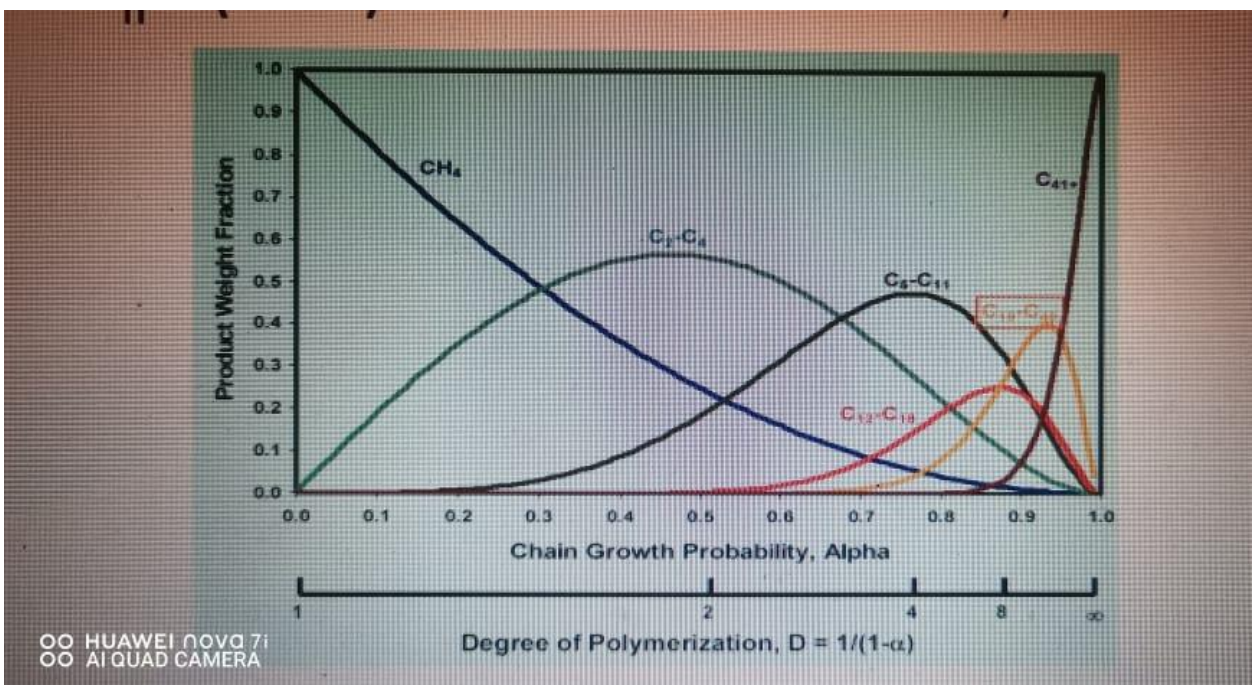
The distribution of N-Paraffin products is determined by the probability that the chain continues to polymerize instead of terminating this probability is defined as **α**

For commercial catalyst **α** varies between 0.5 to 0.90

Product distribution by the Anderson-Schulz-Flory distribution

Weight fraction by carbon number

$-W = (1- \alpha)^2 \alpha^{n-1}$



A kinetic model involving both the FT and the WGS reactions was used to describe the overall performance in the reactor. Reaction rate equations based Langmuir-Hinshelwood-Hougen-Watson models are given by:

RFts= (k_{Fts} P_{co} P_{H2O})/(P_{co}+aP_{H2O})

After loading a catalyst into a reactor the reduction of catalyst was started with a hydrogen gas with flow rate of 30 sccm and nitrogen gas with 10 sccm, nitrogen gas used as a carrier. After reduction at 450 ^{o}C for 4 to 5 hrs then cooling down to 300 ^{o}C in order to promote the reaction at 20 bar under the presence of H_2/CO ratio 1:1. The product gases collected from separator are analyzed by chromatography and hydrocarbons on carbon basis. In Fischer Tropsch process the reaction was started at 300 ^{o}C for a 10 hrs with 20 bar pressure. The flow rate of hydrogen and carbon monoxide was 30 sccm, and nitrogen was 10 sccm which act as an inert. The product is collected into a separator and sends into a distillation column for further purification of hydrocarbons.For these conditions the reactions involved in FT synthesis will be taken as follows:

$$12CO + 25H_2 \rightarrow C_{12}H_{26} + 12H_2O$$

$$13CO + 27H_2 \rightarrow C_{13}H_{28} + 13H_2O$$

$$14CO + 29H_2 \rightarrow C_{14}H_{30} + 14H_2O$$

$$15CO + 31H_2 \rightarrow C_{15}H_{32} + 15H_2O$$

The rate equation for FT reactions is as follows:

$$R_i = 0.278k_i \exp.\left(\frac{-E_i}{RT}\right)^{\cdot} P_{co}^{m} P_{H_2}^{n}$$

The FT hydrocarbon reactions are irreversible but the water shift reaction is reversible so the rate equation which is as follows:

$$R_{WGS} = \frac{k_W\left(P_{CO}P_{H_2} - P_{CO_2}P_{H_2}/K_P\right)}{\left(1+K_1P_{CO}+K_3P_{H_2O}\right)^2}$$

$$k_W = k_5K_1K_3$$

$$logK_p = \left(\frac{P_{CO}P_{H_2}}{P_{CO}P_{H_2O}}\right) = \left(\frac{2073}{T} - 2.029\right)$$

The product gases collected from separator are analyzed by chromatography and hydrocarbons on carbon basis. In Fischer Tropsch process the reaction was started at 300 ^{o}C for a 10 hrs with 20 bar pressure. The flow rate of hydrogen and carbon monoxide was 30 sccm, and nitrogen was 10 sccm which act as an inert. The product is collected into a separator and sends into a distillation column for further purification of hydrocarbons.

Table Kinetic parameters of FT hydrocarbon reactions

M	N	K	E
-1.0784	1.49872	136,783.8	7983.9
0.7622	0.0728	51.556	65,018
-0.5645	1.3155	24.717	49,782
0.4051	0.6635	0.4632	34,885.5
0.4728	1.1389	0.00474	27,728.9
0.8204	0.5026	0.00832	25,730.1
0.5850	0.5982	0.02316	23,564.3

The kinetic parameters of WGS reaction rate equation in the following table.

Table Kinetic parameters of WGS reaction rate equation

K_W(MMOLG^{-1}S^{-1}BAR^{-2})	K_1	K_3(BAR^{-1})
0.21	0.39	3.54

The specification of feed is provided in the paper, units carring the reactions (reactors) specified at specific temperature, pressure and feed flow rate conditions

Details are as follows

The property-method RK-SOAVE is used to evaluate the physical properties of MIXED conventional components and CISOLID components. HCOALGEN and DCOALIGT models are selected for enthalpy and density calculation of nonconventional compounds, correspondingly.

RK Soave Equation

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)}$$

Where,

P= Pressure of Gas, R= Real Gas Constant,

T= Temperature, V_m= molar volume,

a and b= constants that corrects for attractive potential of molecules and volume. The details of a and b constants can be obtained from literature.

The HCOALGEN model for enthalpy calculation involves element characteristics for non-conventional compounds:

- Proximate analysis results (PROXANAL in Aspen Plus)
- Ultimate analysis results (ULTANAL in Aspen Plus)
- Sulfur analysis results (SULFANAL in Aspen Plus)

The DCOALIGT model for density calculation requires two component attributes ULTANAL and SULFANAL. Properties of char and ash produced in gasification of coal same methodology is applied as mentioned above and similar models are employed to evaluate enthalpy and density.

- Ultimate and Proximate analysis

Block Description

Components specified in the model were taken from component databanks Pure27, AQUEOUS, SOLIDS and INORGANIC. The molecular structure of components is being used as defined in Aspen plus.C_6H_6 was used define tar produced in pyrolysis block which also represents the number of higher hydrocarbons. The heavy mass organic compounds like tar, phenol, naphtha and oil are referred to as distillable organic liquids. The heavy molecular weight hydrocarbons produced during gasification and combustion of char have very small compositions and possess properties that of liquid at ambient conditions

After drying, water vapors and dry coal enters into a gas-solid separator, SEP-1. The detached vapors are amalgamated in gas stream from coal pyrolysis, char gasification, and char combustion to produce the final syngas. DRY-COAL goes into pyrolysis block. In the process flow diagram line for heat Q-DRYING exhibited for heating purpose that is homogenous heating atmosphere in the gasifier. The coal pyrolysis evolves lot of heat which is used in drying, char gasification, and char combustion

Table Gas Cleaning Units

Parameters	Absorber	Stripper
Temperature ^{o}C	35	82
Pressure (Bar)	35	2
Flow Rate (Kmol/hr)	6512	1511
Distillate Flow Rate	1200 Kmol/hr	
Reboiler Duty	47870000 Watt	
Number of Stages	20	