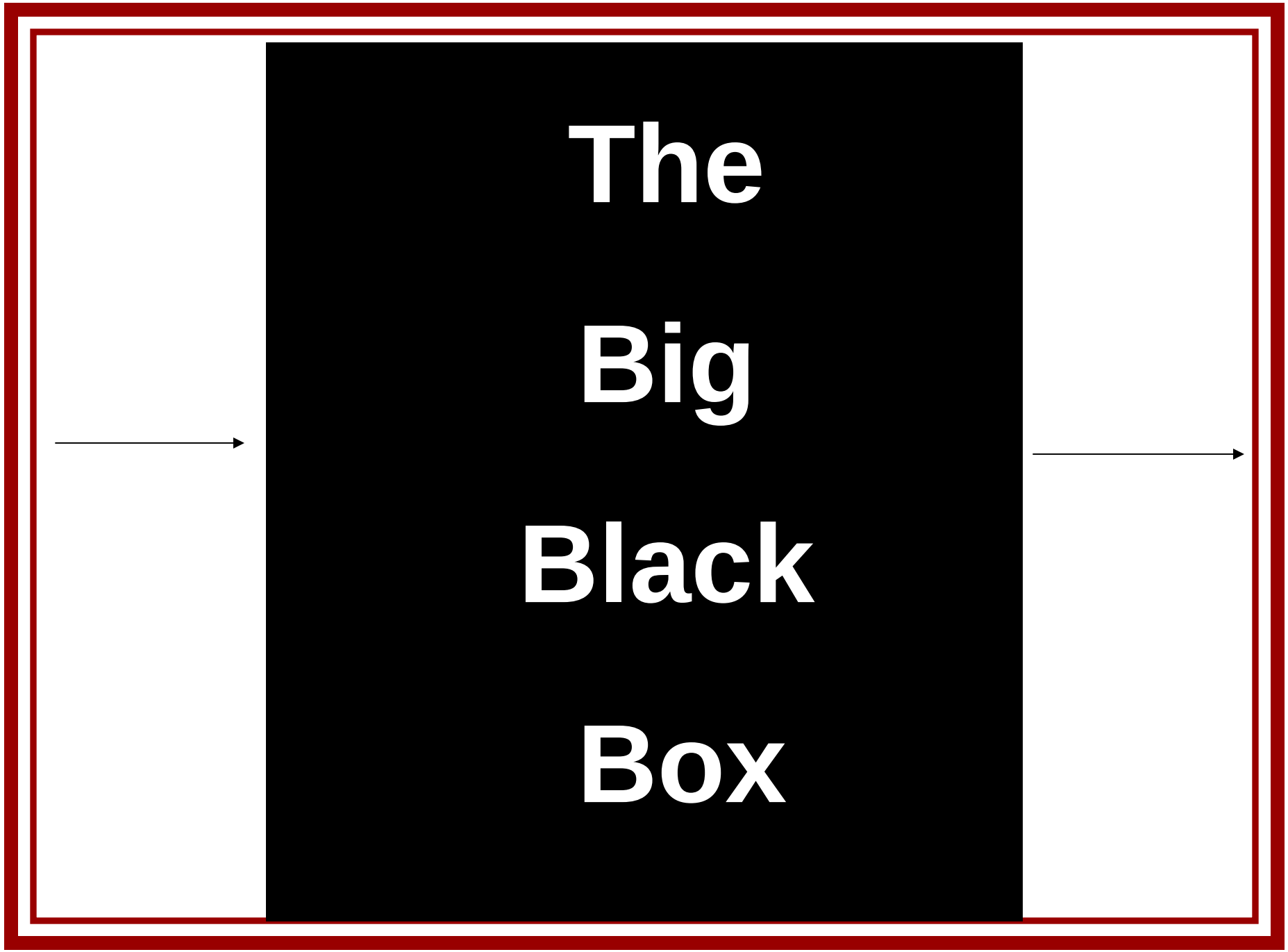
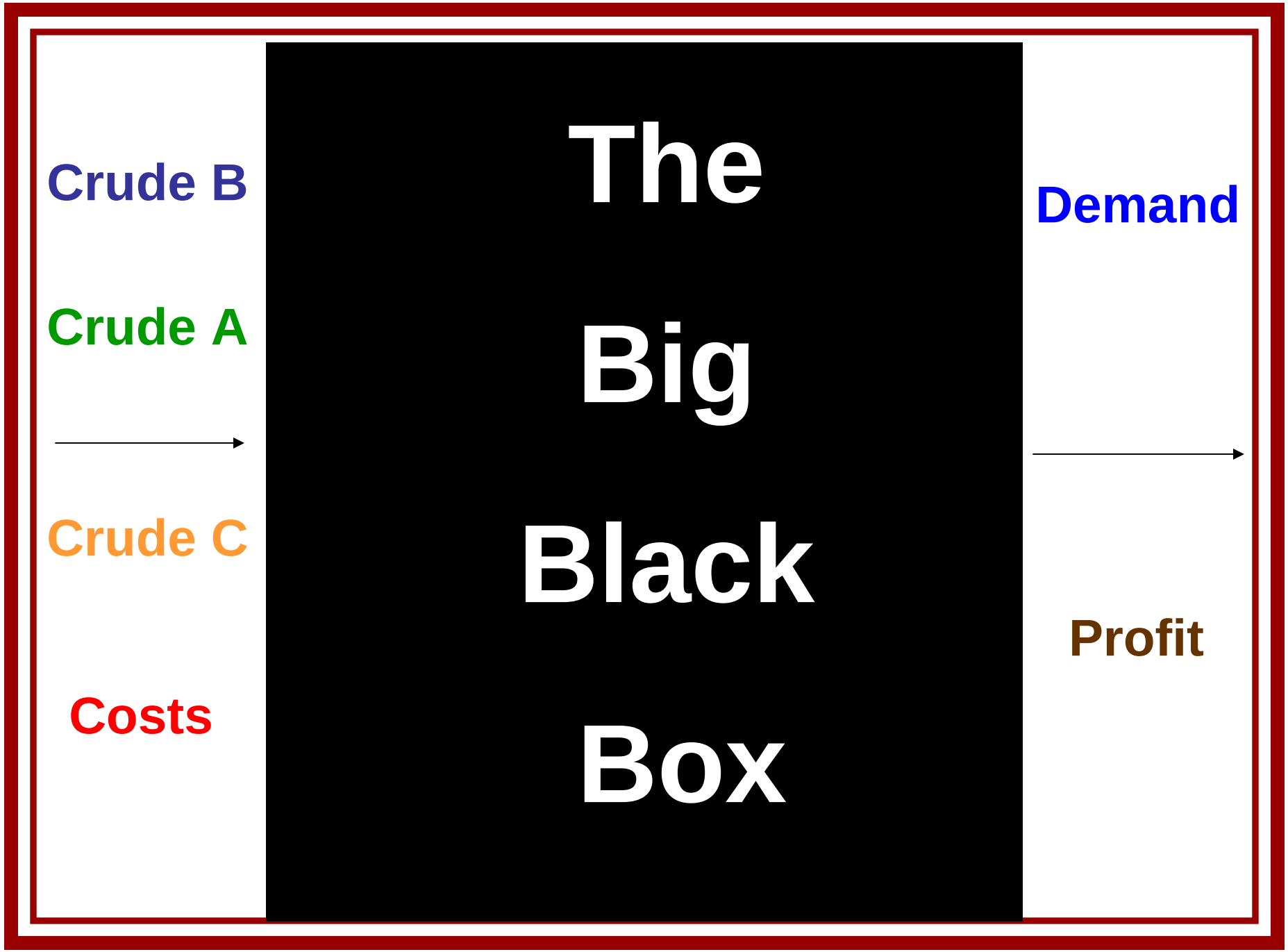
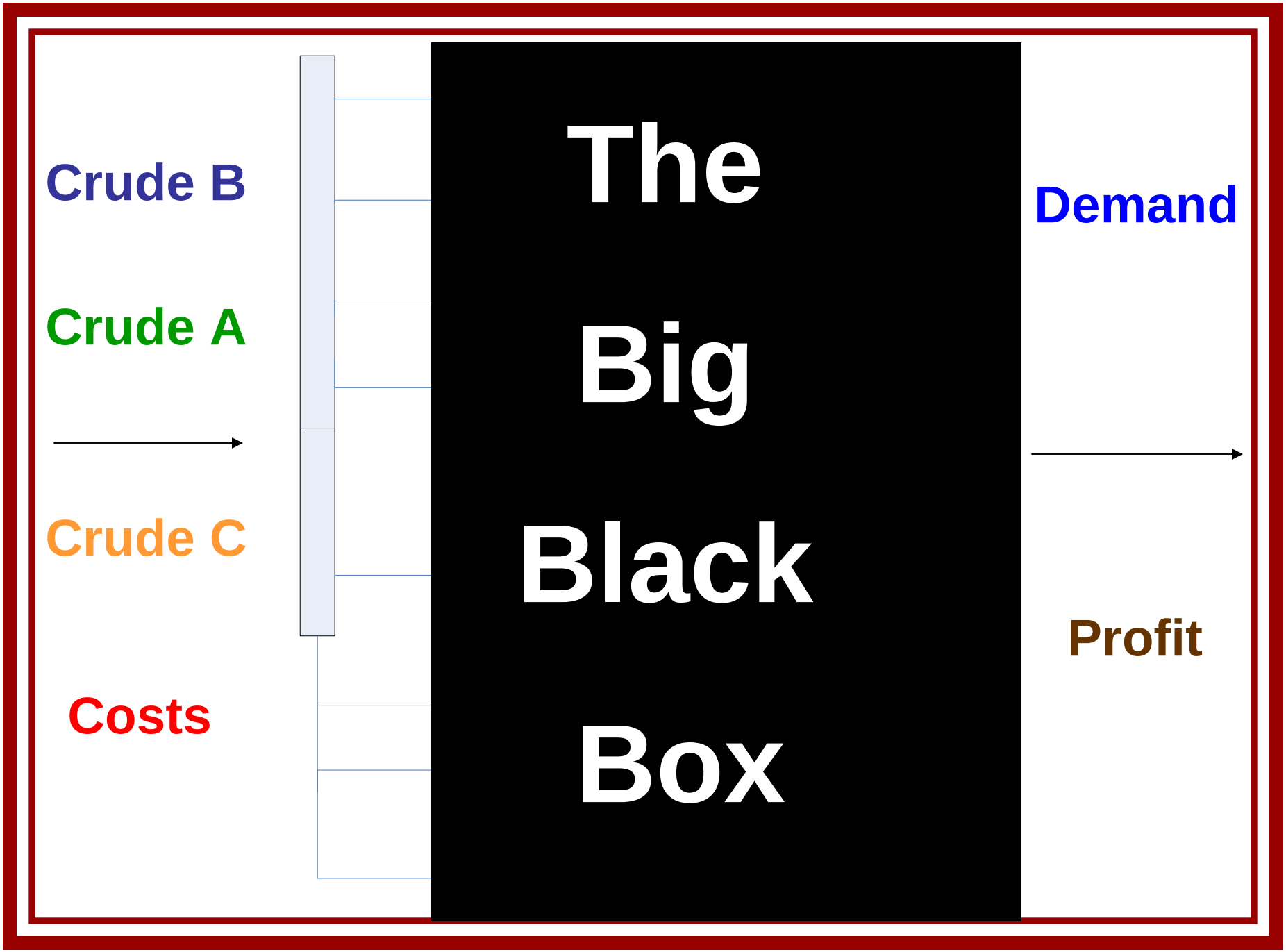
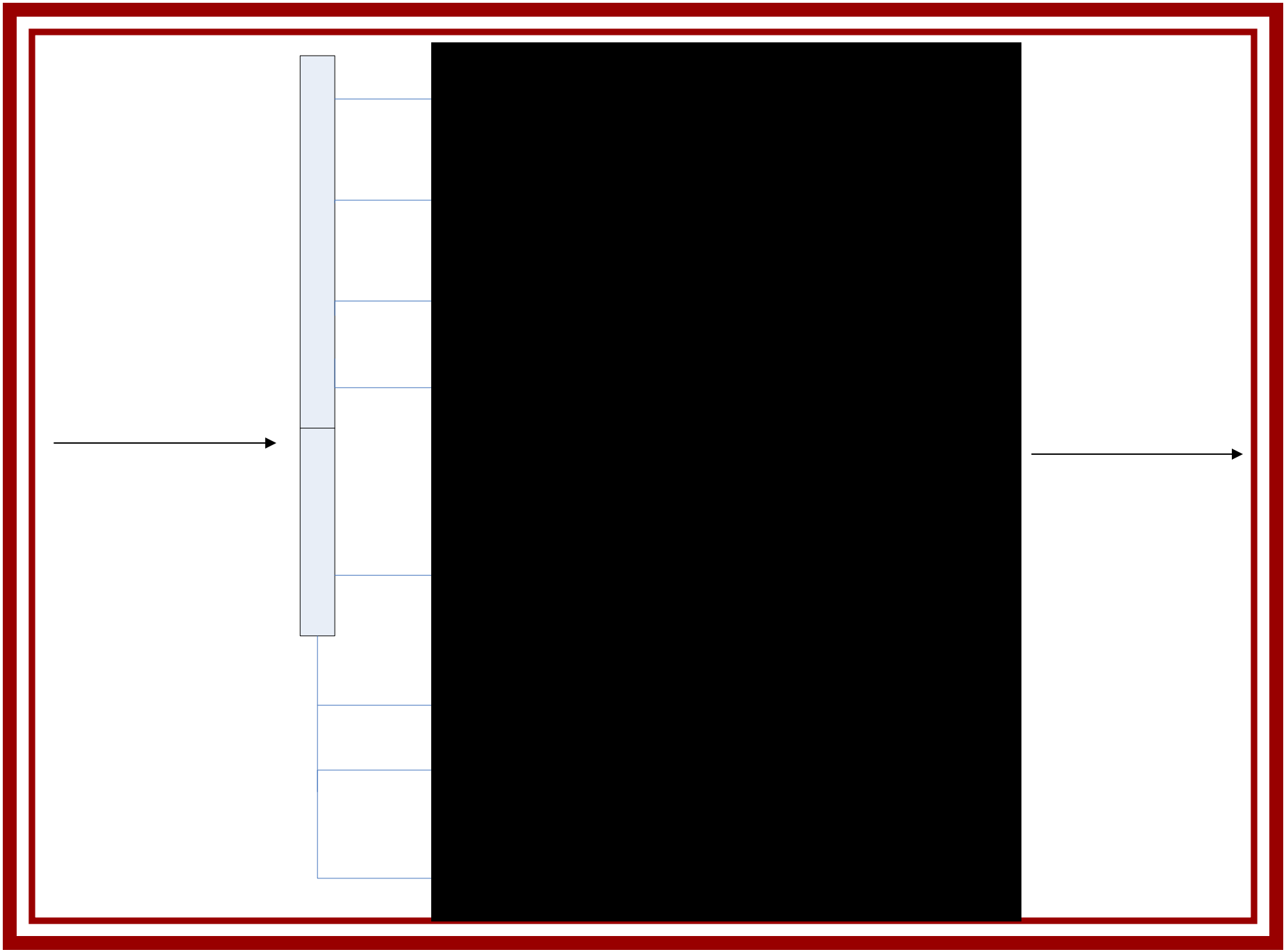
Refinery Modeling

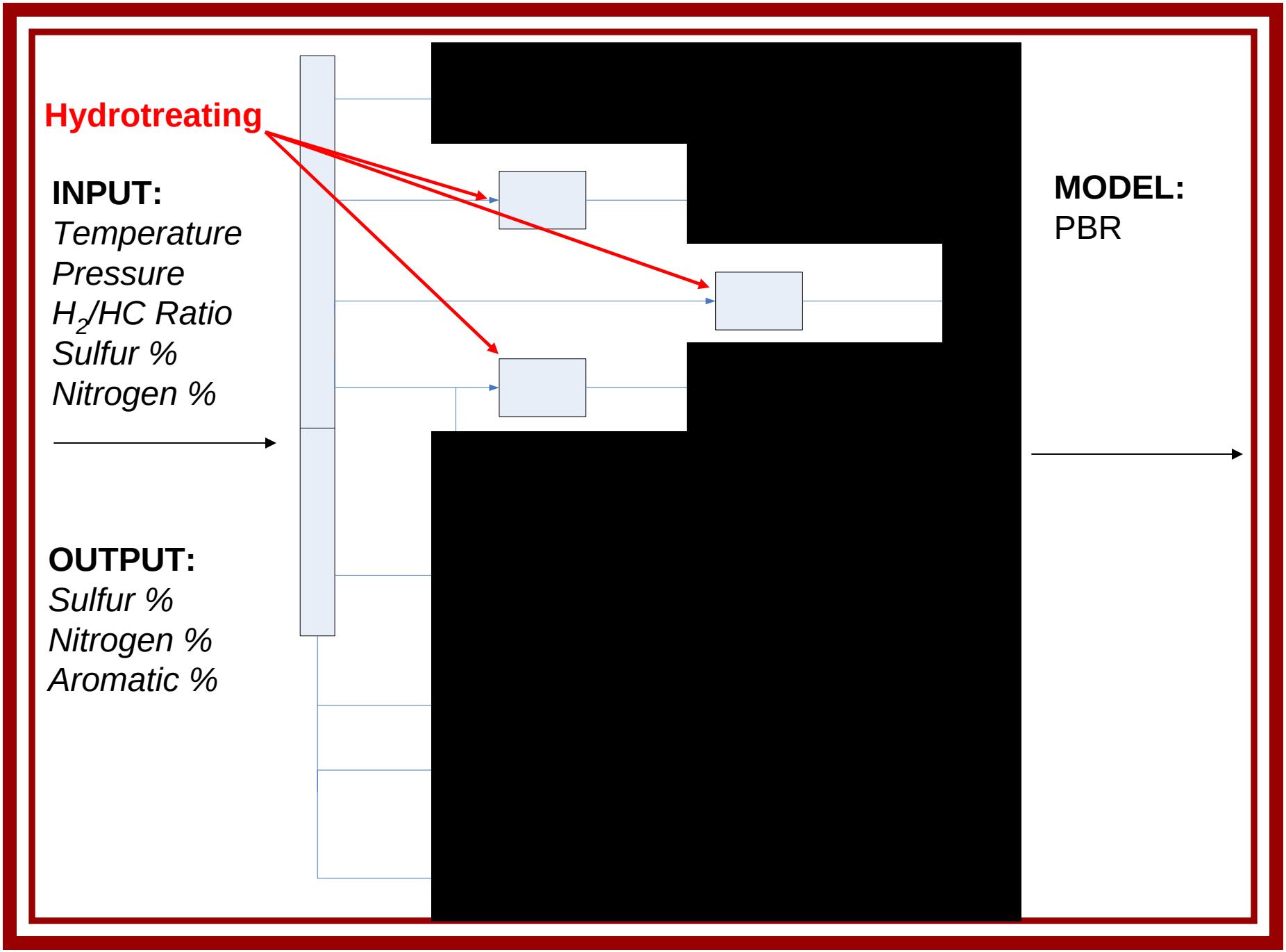
Aaron Smith, Michael Frow,
Joe Quddus, Donovan Howell,
Thomas Reed, Clark Landrum,
Brian Clifton
May 2, 2006

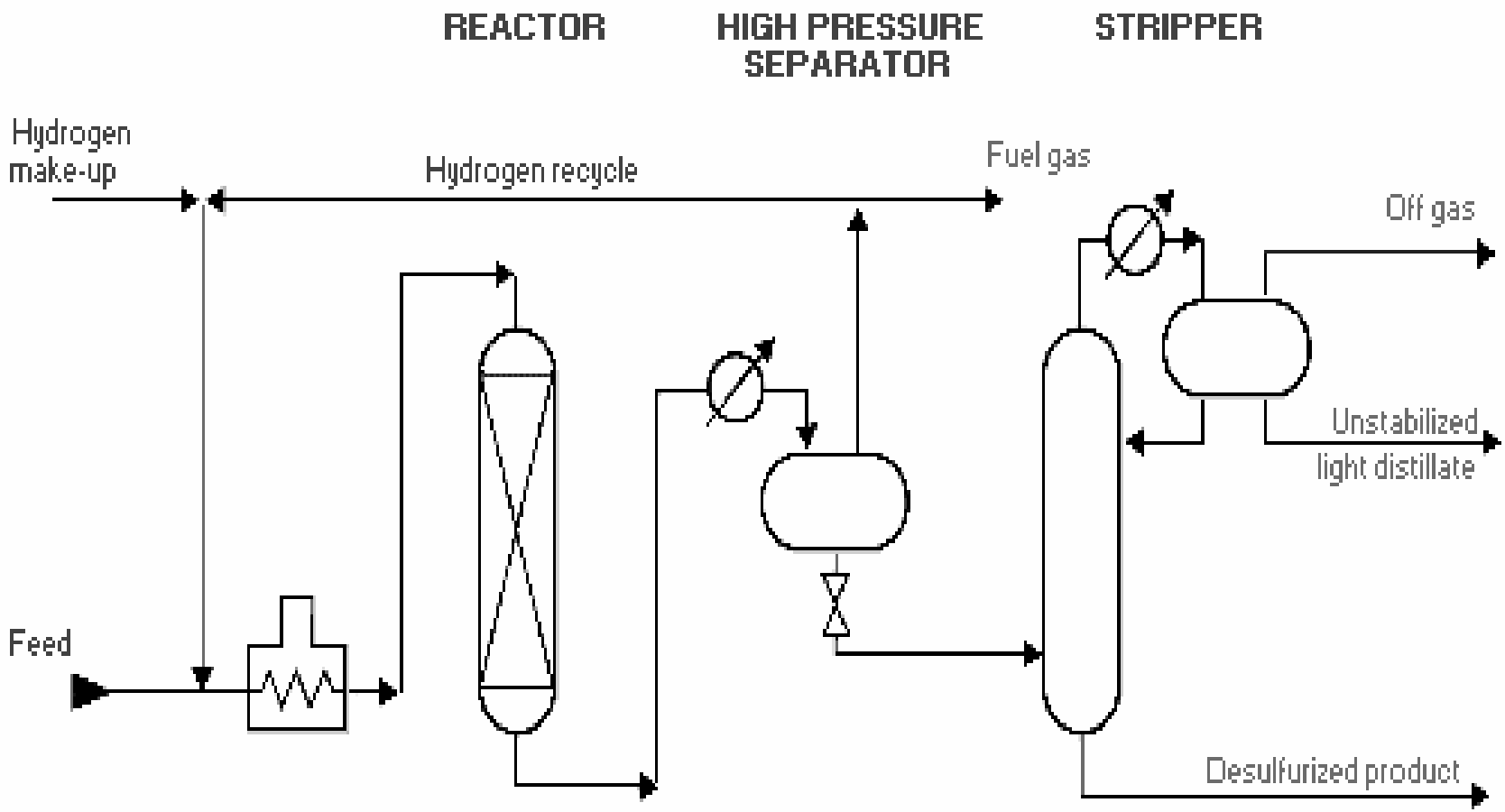

The
Big
Black
Box


Crude B
Crude A
Crude C
Costs
The
Big
Black
Box
Demand
Profit


Crude B
Crude A
Crude C
Costs
The
Big
Black
Box
Demand
Profit



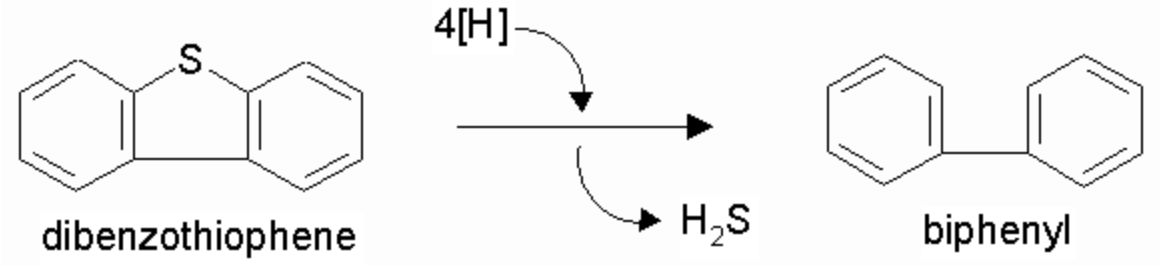

Hydrotreating
INPUT:
Temperature
Pressure
H2/HC Ratio
Sulfur %
Nitrogen %
OUTPUT:
Sulfur %
Nitrogen %
Aromatic %
MODEL:
PBR



http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2fig25.gif

Hydrotreating

- Removal of sulfur, nitrogen, and aromatics.
- Government regulations are leading to increased sulfur removal requirements.

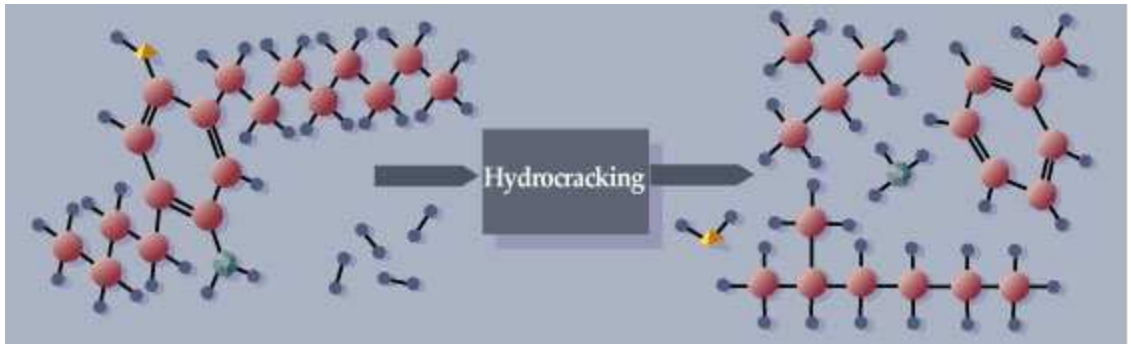


Typical Processing Conditions

	Space velocity	H_2/HC	H_2 Pressure (psia)	Temperature (^oC)
Naptha	1.0-5.0	300	200	290
Middle Distillate	1.0-4.0	800	400	330
Light Gas Oil	0.7-1.5	1500	700	425
Heavy Gas Oil	0.75-2.0	2000	800	355

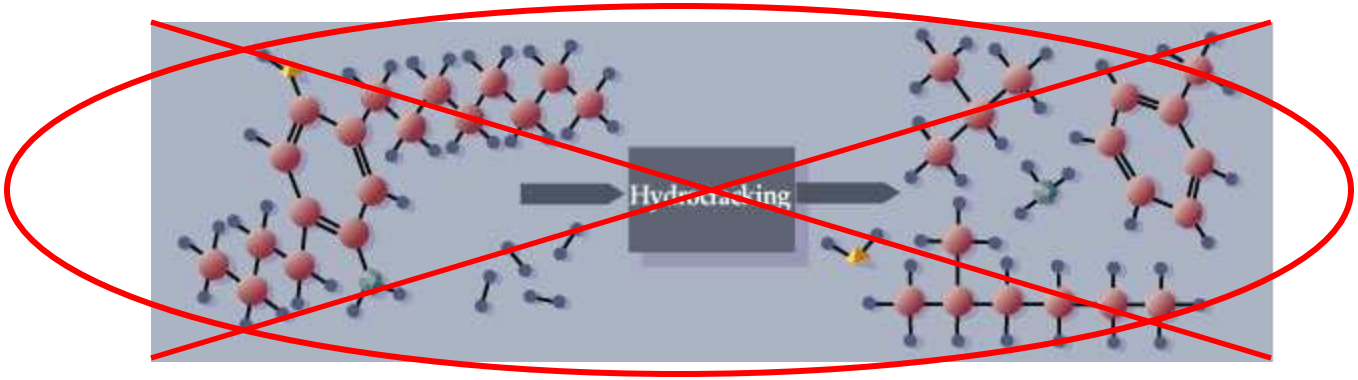
Hydrotreating

- Cracking is assumed to be insignificant.
  - Therefore, properties such as density and molecular weight are assumed to be constant.



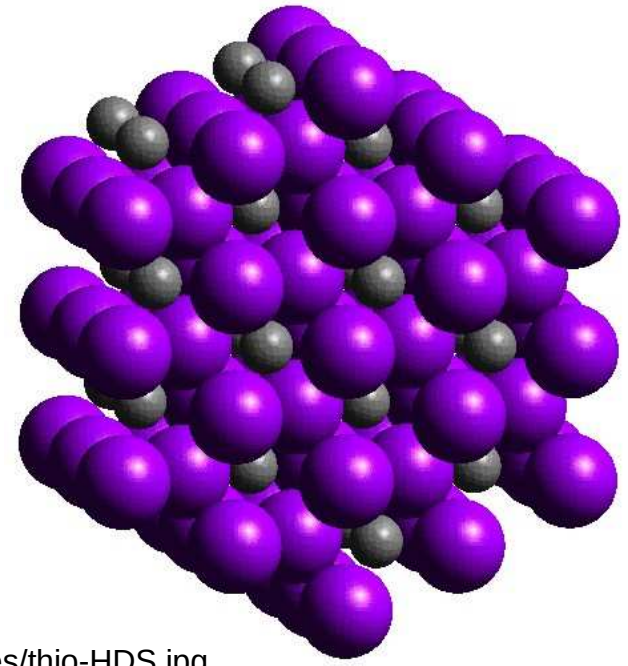
Hydrotreating

- Cracking is assumed to be insignificant.
  - Therefore, properties such as density and molecular weight are assumed to be constant.

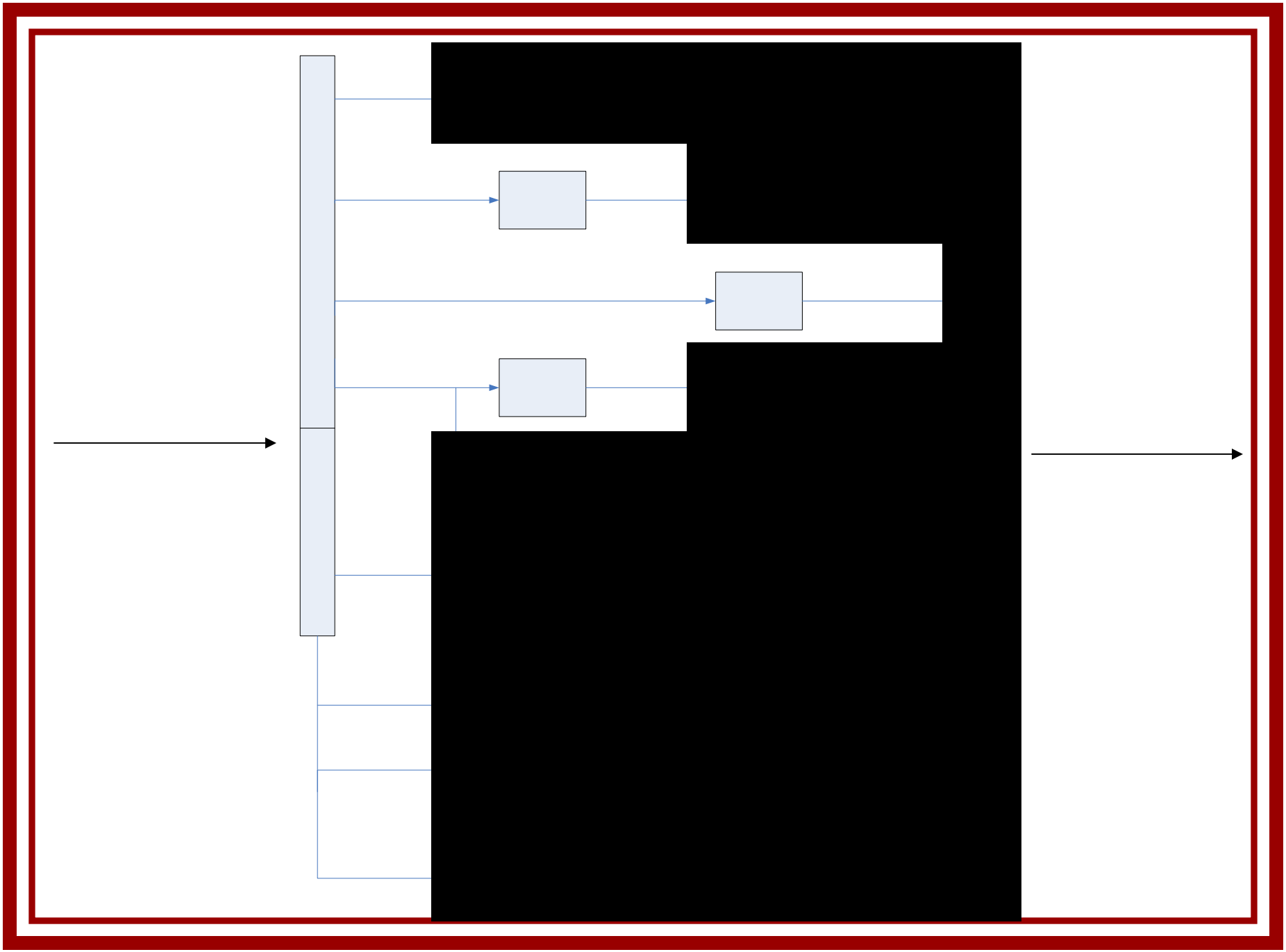


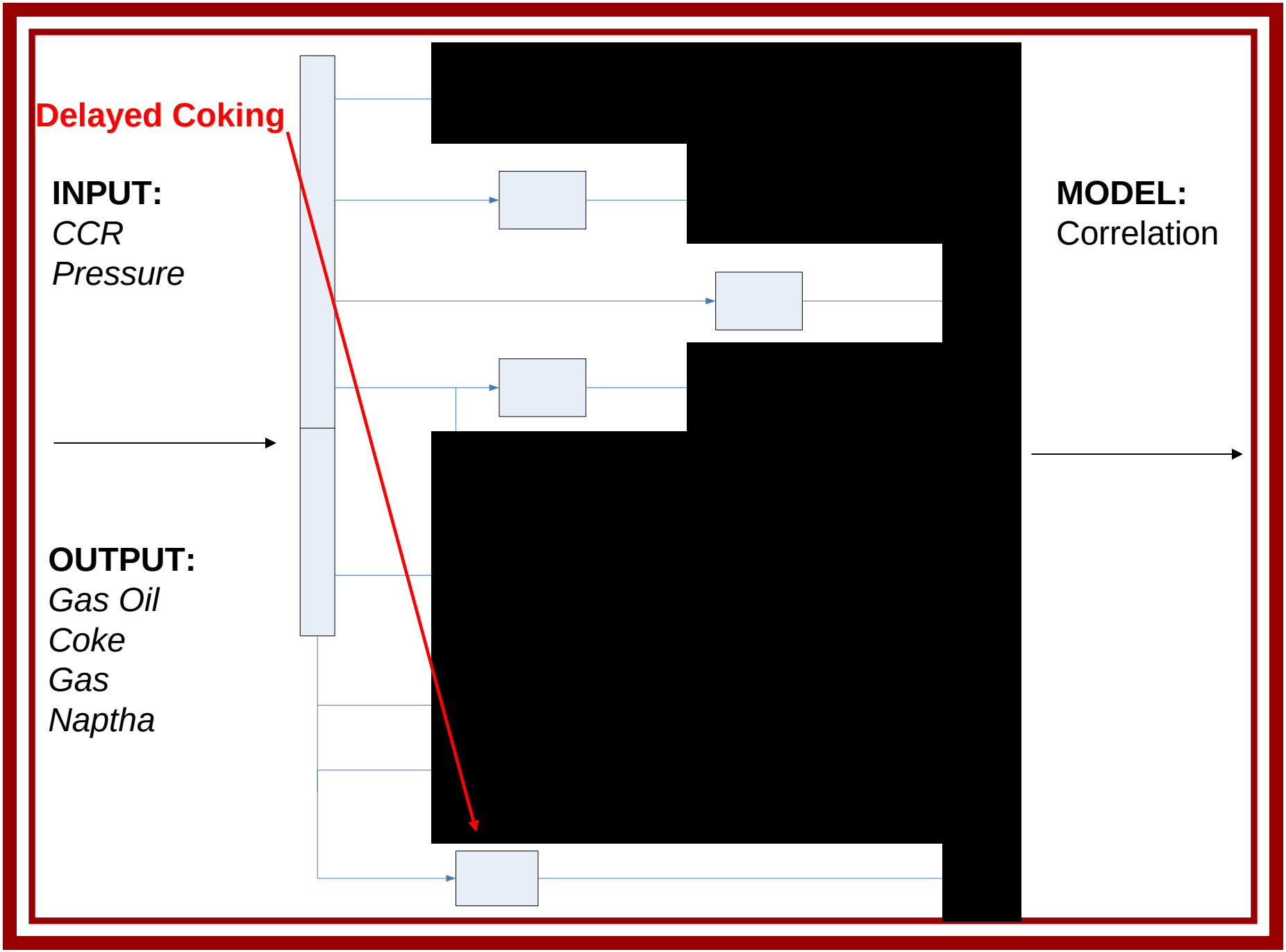
Hydrotreating Model

- For MoCo catalyst reaction rates are:
  - $Rate_s = k_s C_s^{2} C_{H2}^{.75}$
  - $Rate_n = k_n C_n^{1.4} C_{H2}^{.6}$
  - $Rate_{ar} = k_{ar} C_{ar} C_{H2}$



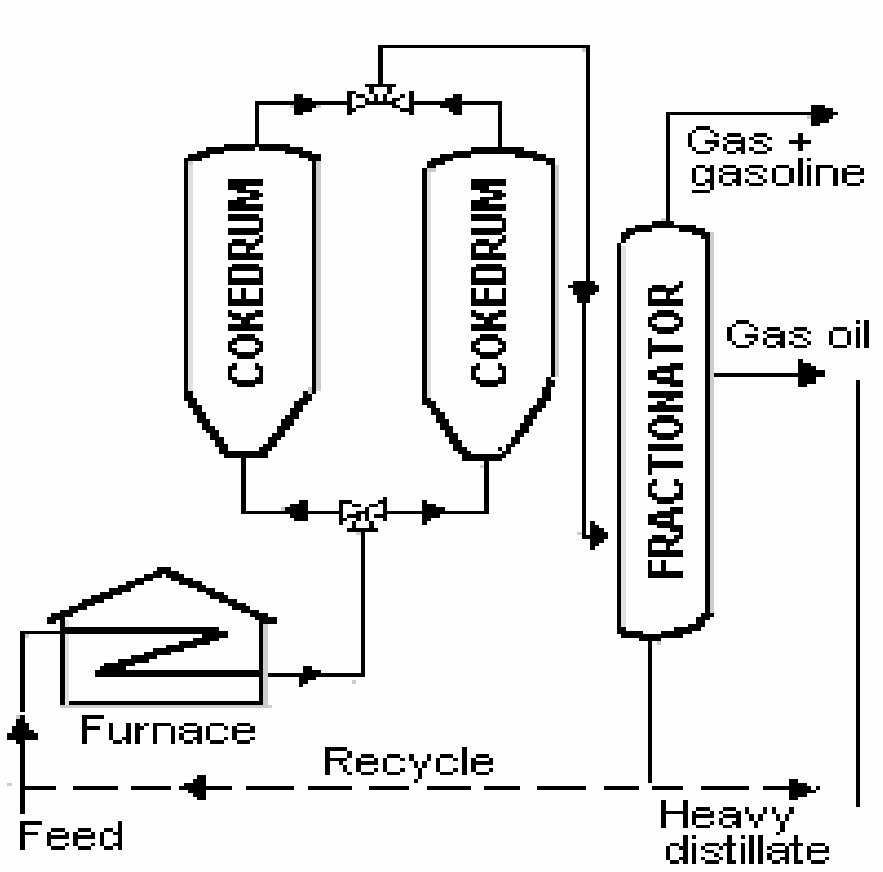
http://www.chem.wwu.edu/dept/facstaff/bussell/research/images/thio-HDS.jpg




Delayed Coking
INPUT:
CCR
Pressure
MODEL:
Correlation
OUTPUT:
Gas Oil
Coke
Gas
Naptha

Delayed Coking

- Used to process bottoms from the vacuum distillate.
- Breaks down this portion into usable napthas, gas, and gas oil.



Delayed Coking

- Coke Products
  - Shot Coke
  - Sponge Coke
  - Needle Coke

Delayed Coking Model

- Most important parameter is the Conradson Carbon Residue.
  - *Coke = 1.6 x CCR*
  - *Gas = 7.8 + .144 x CCR*
  - *Naptha = 11.29 + .343 x CCR*
  - *Gas oil = 100 – Coke – Gas - Naptha*
- This is an estimate from Gary and Handwerk

Effect of Pressure on Product

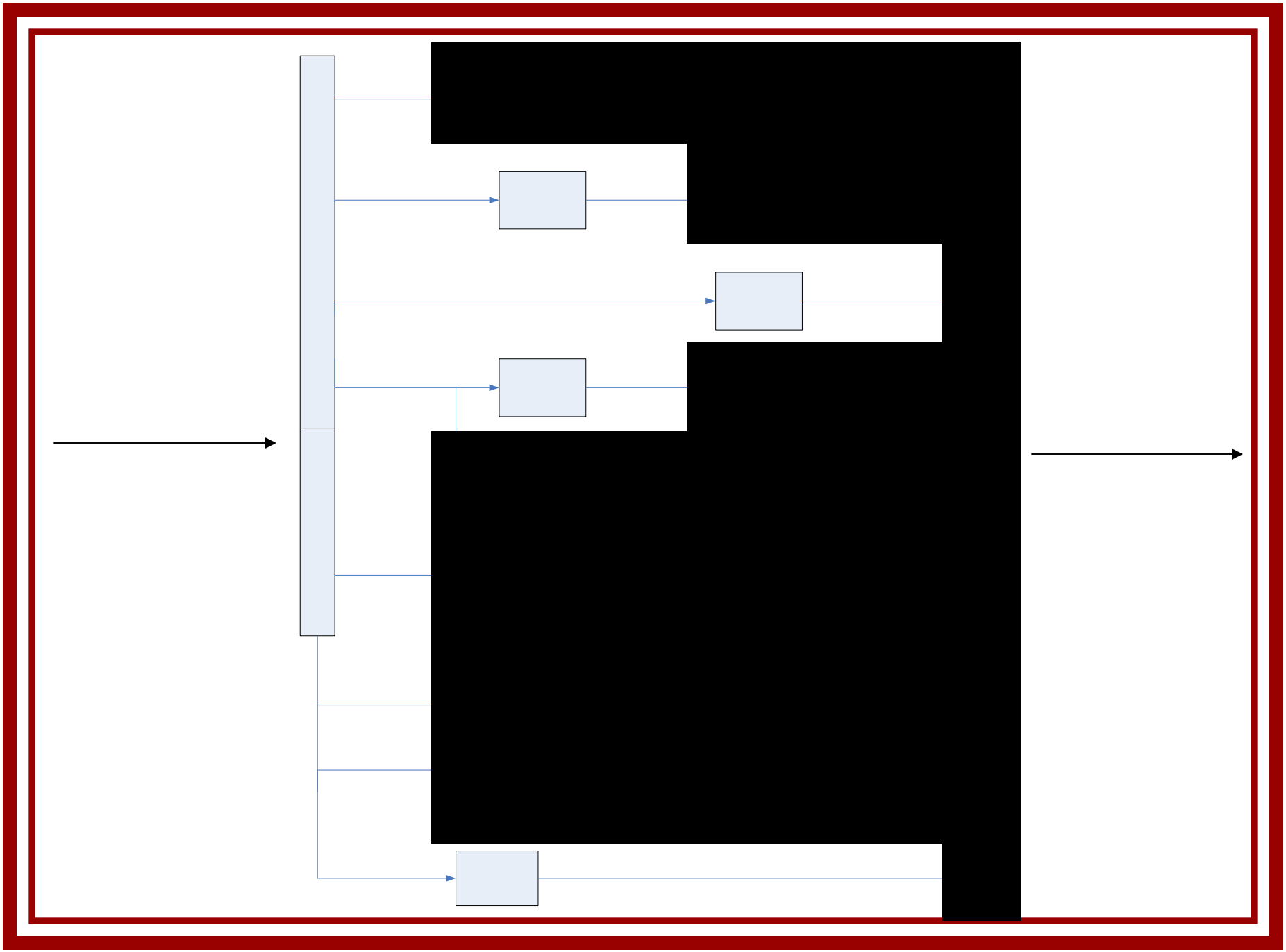
	CCR (wt%)	18.1	
	Correlation	15 psig	35 psig
Coke	29	27.2	30.2
Gas Yield	10.4	9.1	9.9
Naptha Yield	17.5	12.5	15
Gas Oil Yield	43.1	51.2	44.9

Delayed Coking Model

- Modified Equations
  - *Gas = (7.4 + (.1 x CCR)) + (.8 x (P-15)/20)*
  - *Naptha = (10.29 + (.2 x CCR)) + (2.5 x (P-15)/20)*
  - *Coke = (1.5 x CCR) + (3 x (P-15)/20)*
  - *Gas oil = 100 – Gas – Naptha - Coke*

New Correlation

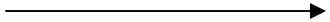
	CCR (wt%)	18.1		
	Correlation (15 psig)	Correlation (35 psig)	15 psig	35 psig
Coke	27.2	30.2	27.2	30.2
Gas Yield	9.2	10.0	9.1	9.9
Naptha Yield	13.9	16.4	12.5	15
Gas Oil Yield	49.7	43.4	51.2	44.9



Catalytic Reforming

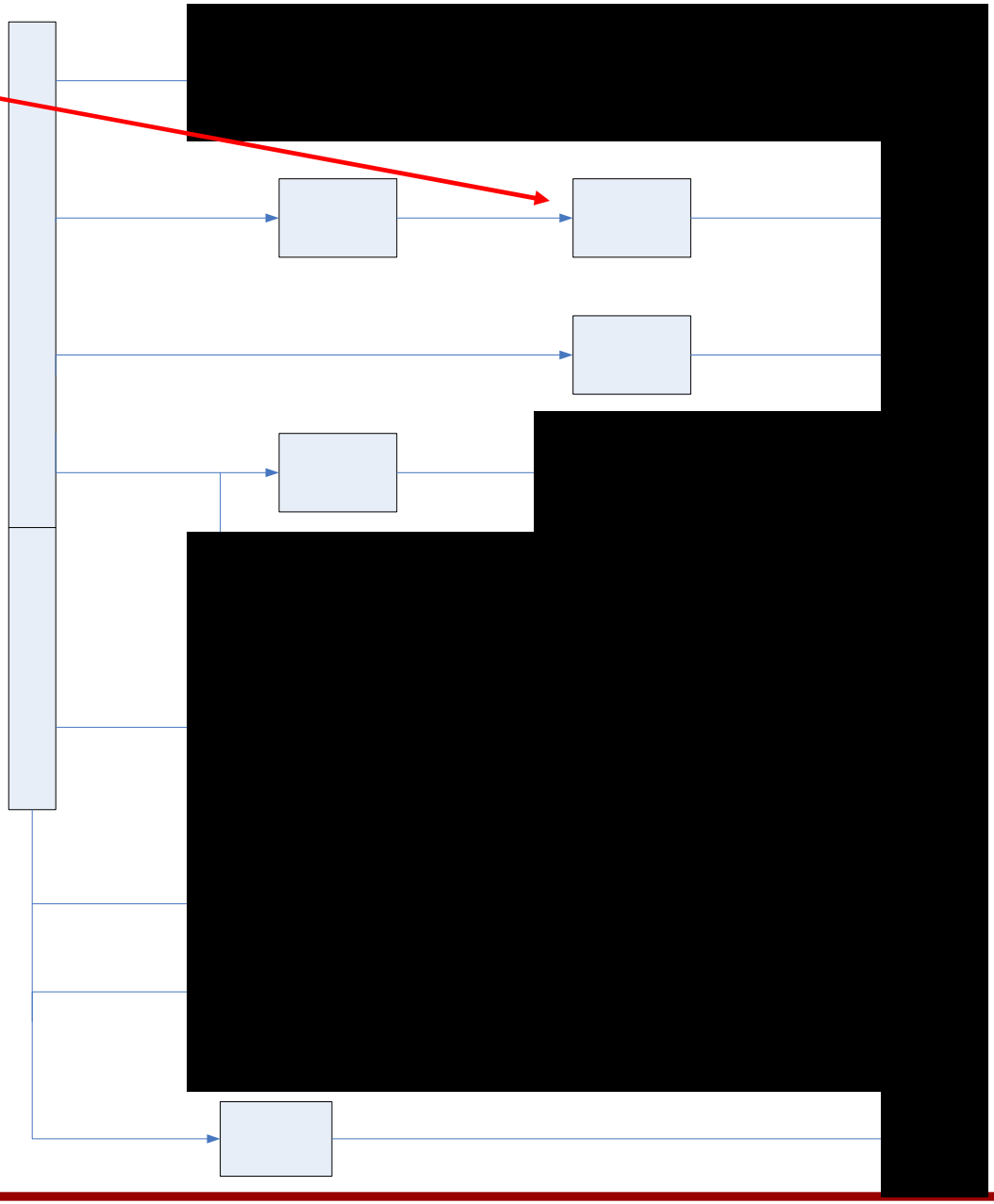
INPUT:

Temperature
Pressure
% Napthenes
% Aromatics
% Paraffins

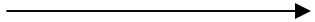


OUTPUT:

Hydrogen
LPG
Reformate



MODEL:
PBR



Catalytic Reforming

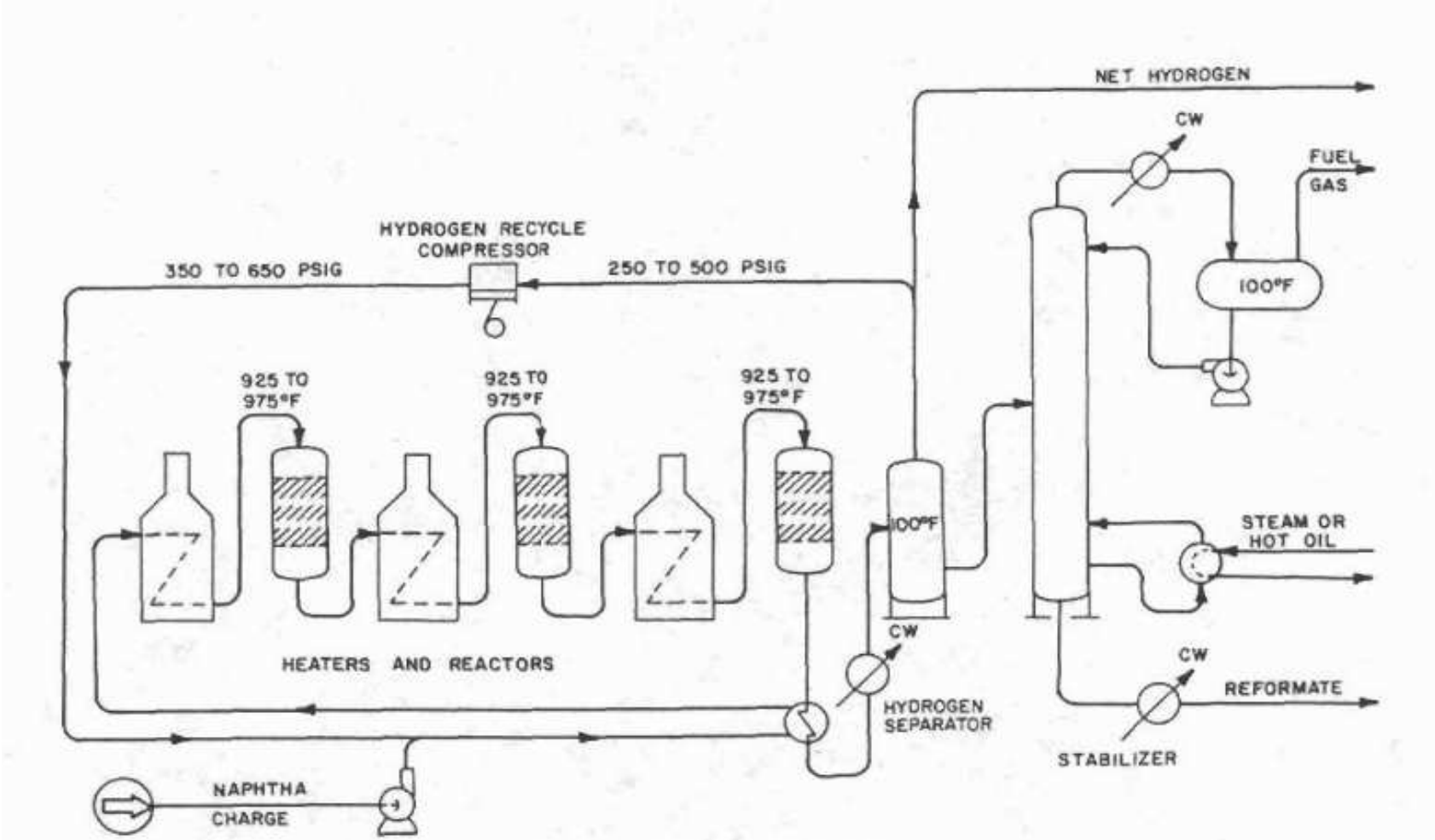


FIG. 6.1. Catalytic reforming

Catalytic Reforming

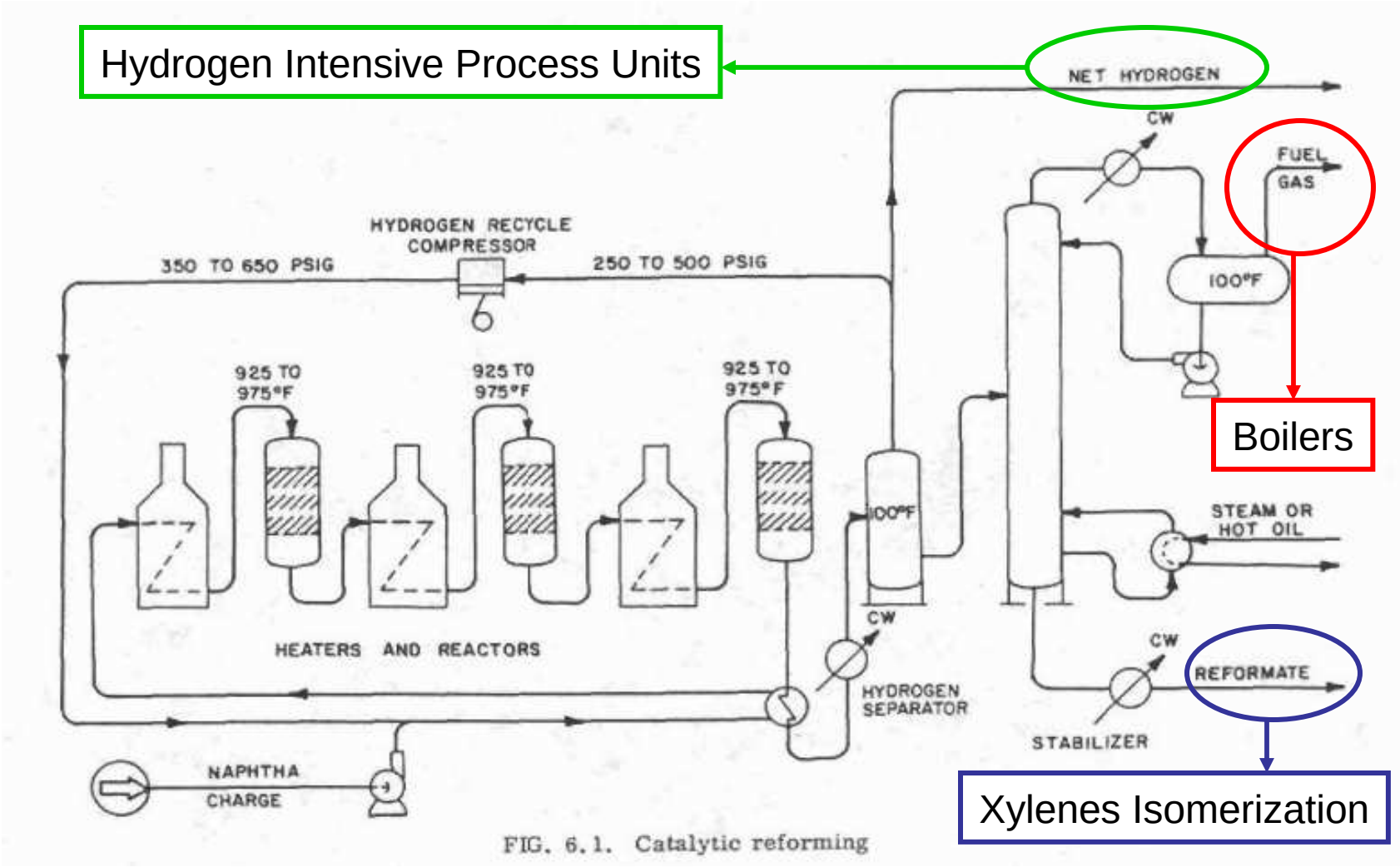


FIG. 6.1. Catalytic reforming

Catalytic Reforming

- Simplified reactions and equations from Case Study 108 by Rase

$$(1) Napthenes \longleftrightarrow aromatics + 3 * H_2$$

$$(2) Paraffins \longleftrightarrow napthenes + H_2$$

$$(3) Hydrocracking\_of\_paraffins$$

$$(4) Hydrocracking\_of\_napthenes$$

Catalytic Reforming

$$(1) C_nH_{2n} \longleftrightarrow C_nH_{2n-6} + 3H_2$$

$$(2) C_nH_{2n+2} \longleftrightarrow C_nH_{2n} + H_2$$

$$(3) C_nH_{2n+2} + \left(\frac{n-3}{3}\right)H_2 \longrightarrow \frac{n}{15}C_1 + \frac{n}{15}C_2 + \frac{n}{15}C_3 + \frac{n}{15}C_4 + \frac{n}{15}C_5$$

$$(4) C_nH_{2n} + \frac{n}{3}H_2 \longrightarrow \frac{n}{15}C_1 + \frac{n}{15}C_2 + \frac{n}{15}C_3 + \frac{n}{15}C_4 + \frac{n}{15}C_5$$

Catalytic Reforming

$$\hat{k}_{P1} = \exp\left(23.21 - \frac{34750}{T}\right), [=] \frac{moles}{(hr)(lb\_cat.)(atm)}$$

$$K_{P1} = \frac{P_A * P_H^3}{P_N} = \exp\left(46.15 - \frac{46045}{T}\right), [=] atm^3$$

$$\hat{k}_{P2} = \exp\left(35.98 - \frac{59600}{T}\right), [=] \frac{moles}{(hr)(lb\_cat.)(atm)^2}$$

$$K_{P2} = \frac{P_P}{P_N * P_H} = \exp\left(\frac{8000}{T} - 7.12\right), [=] atm^{-1}$$

$$\hat{k}_{P3} = \hat{k}_{P4} = \exp\left(42.97 - \frac{62300}{T}\right), [=] \frac{moles}{(hr)(lb\_cat.)}$$

Catalytic Reforming

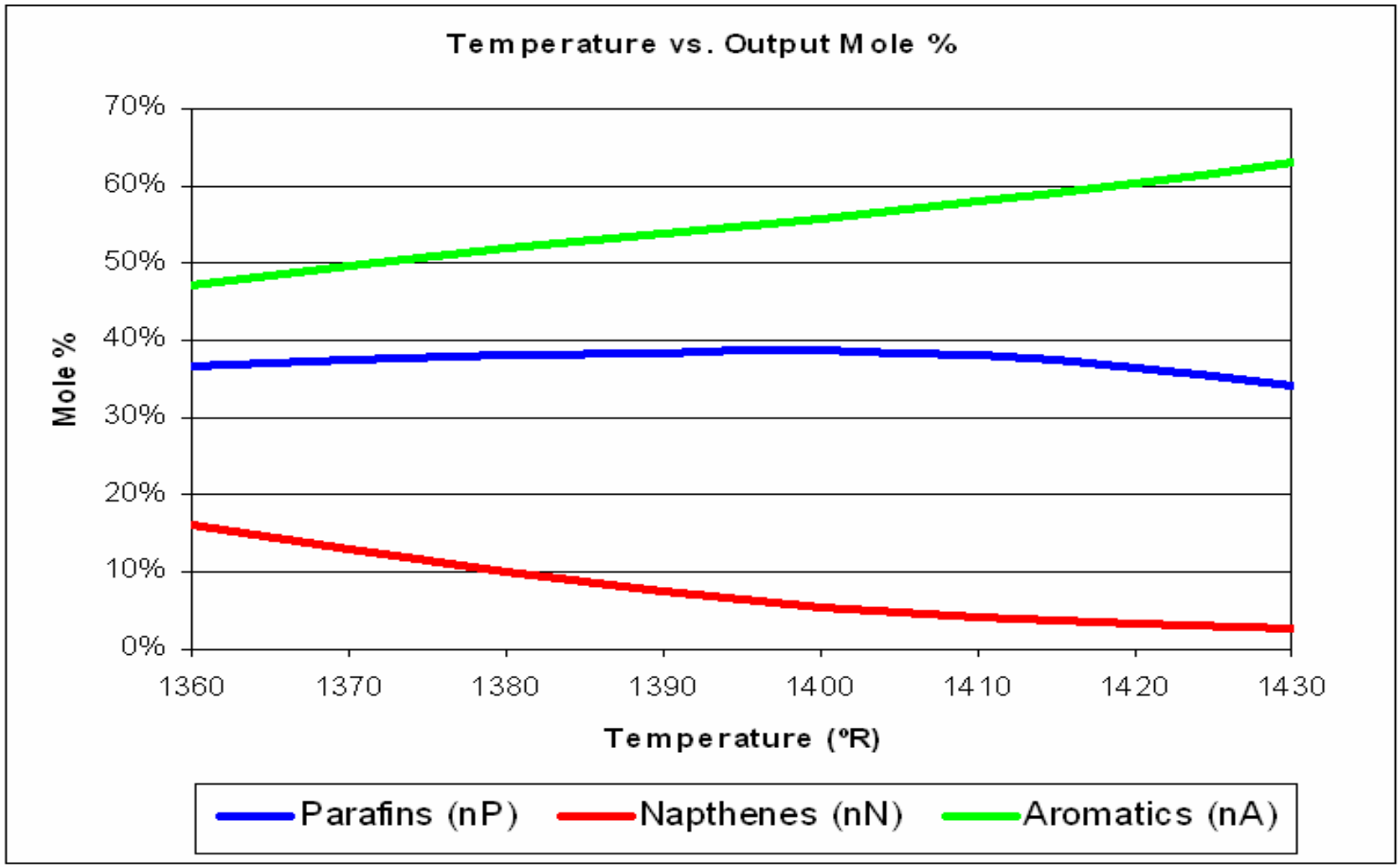
$$-\hat{r}_1 = \hat{k}_{P1}\left(P_N - \frac{P_A * P_H{}^3}{K_{P1}}\right)[=]\frac{moles\_napthene\_converted\_to\_aromatics}{(hr)(lb\_cat.)}$$

$$-\hat{r}_2 = \hat{k}_{P2}\left(P_N * P_H - \frac{P_P}{K_{P2}}\right)[=]\frac{moles\_napthene\_converted\_to\_paraffins}{(hr)(lb\_cat.)}$$

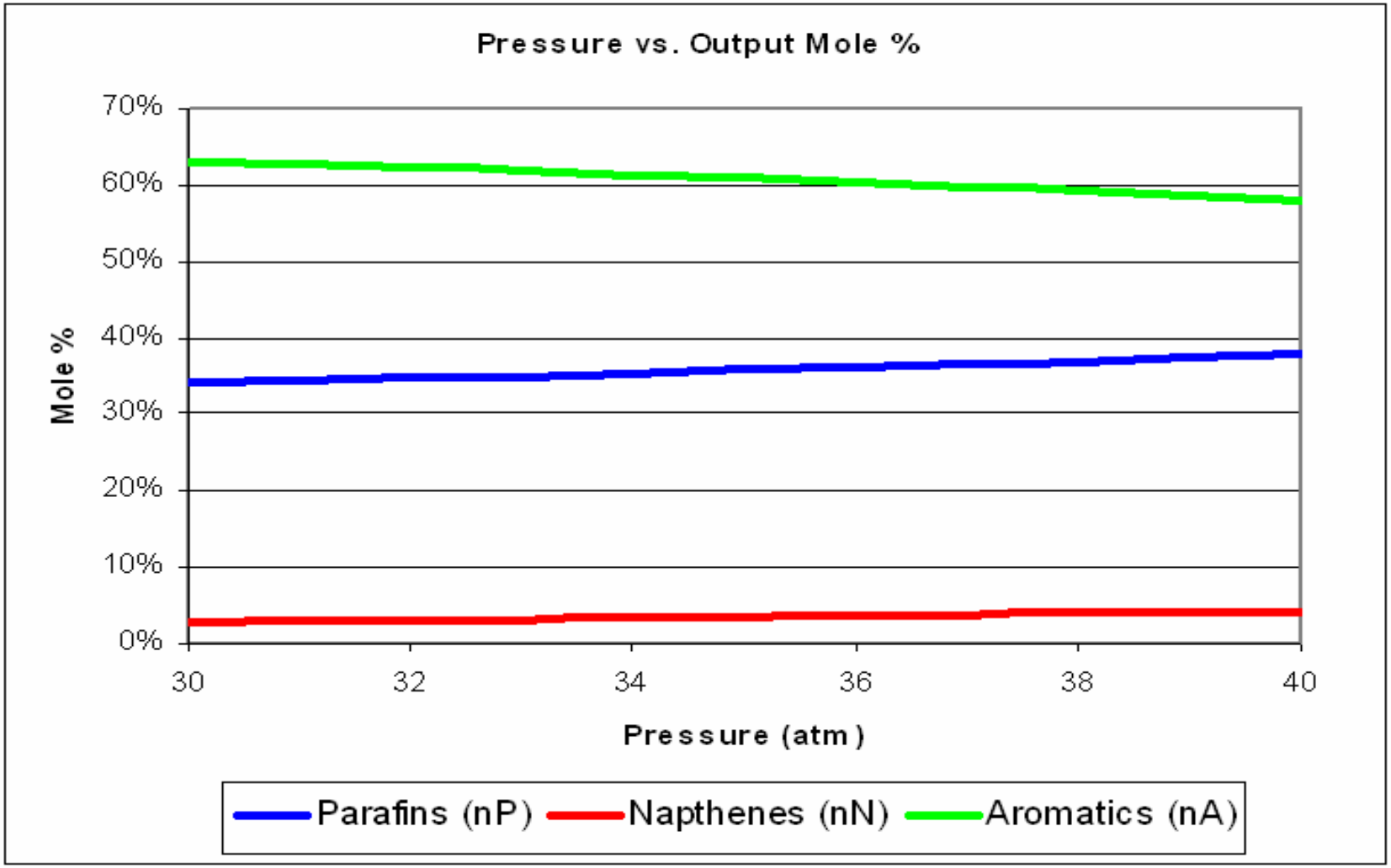
$$-\hat{r}_3 = \hat{k}_{P3}\left(\frac{P_P}{P}\right)[=]\frac{moles\_paraffins\_converted\_by\_hydrocracking}{(hr)(lb\_cat.)}$$

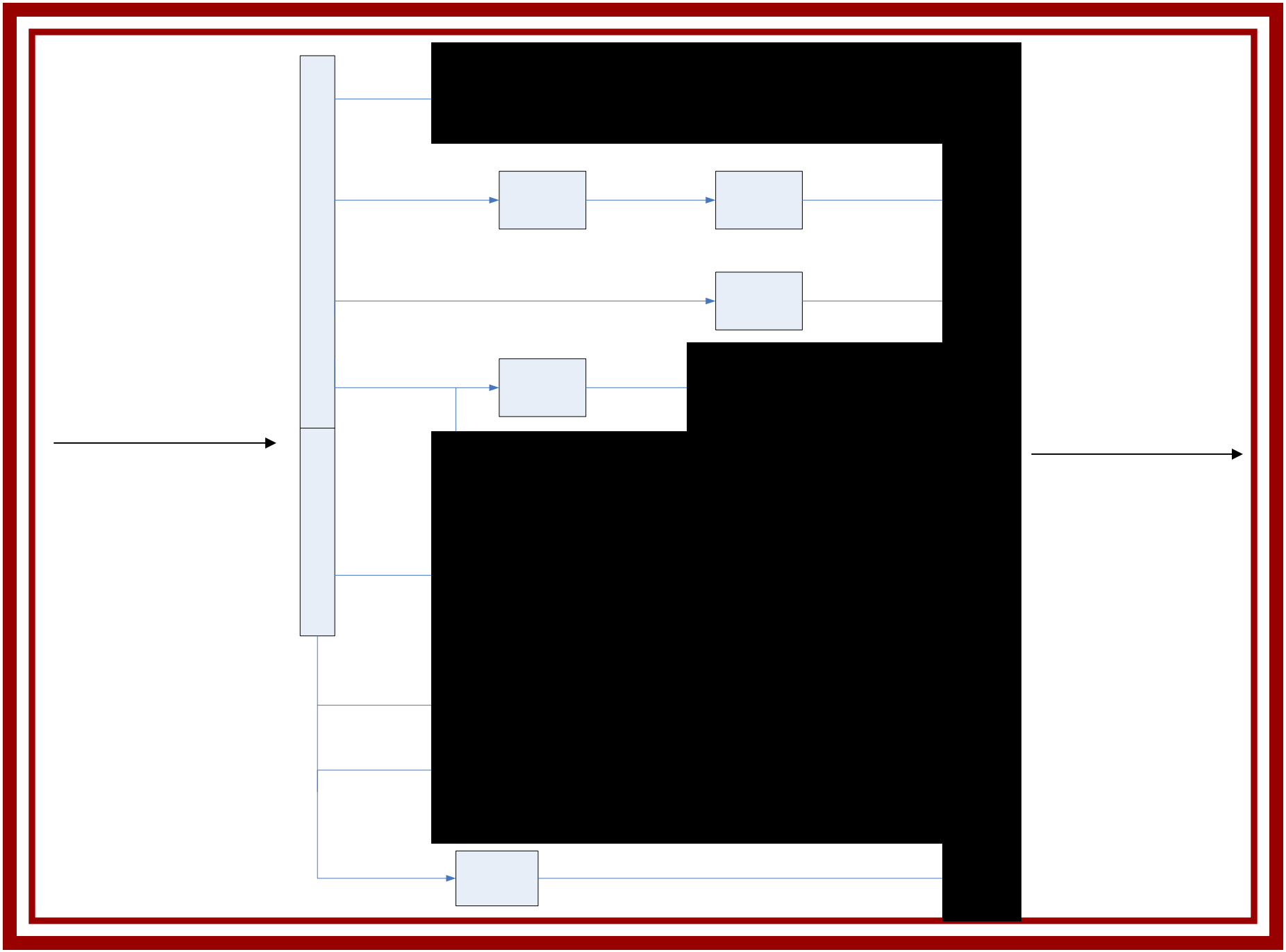
$$-\hat{r}_4 = \hat{k}_{P4}\left(\frac{P_N}{P}\right)[=]\frac{moles\_napthenes\_converted\_by\_hydrocracking}{(hr)(lb\_cat.)}$$

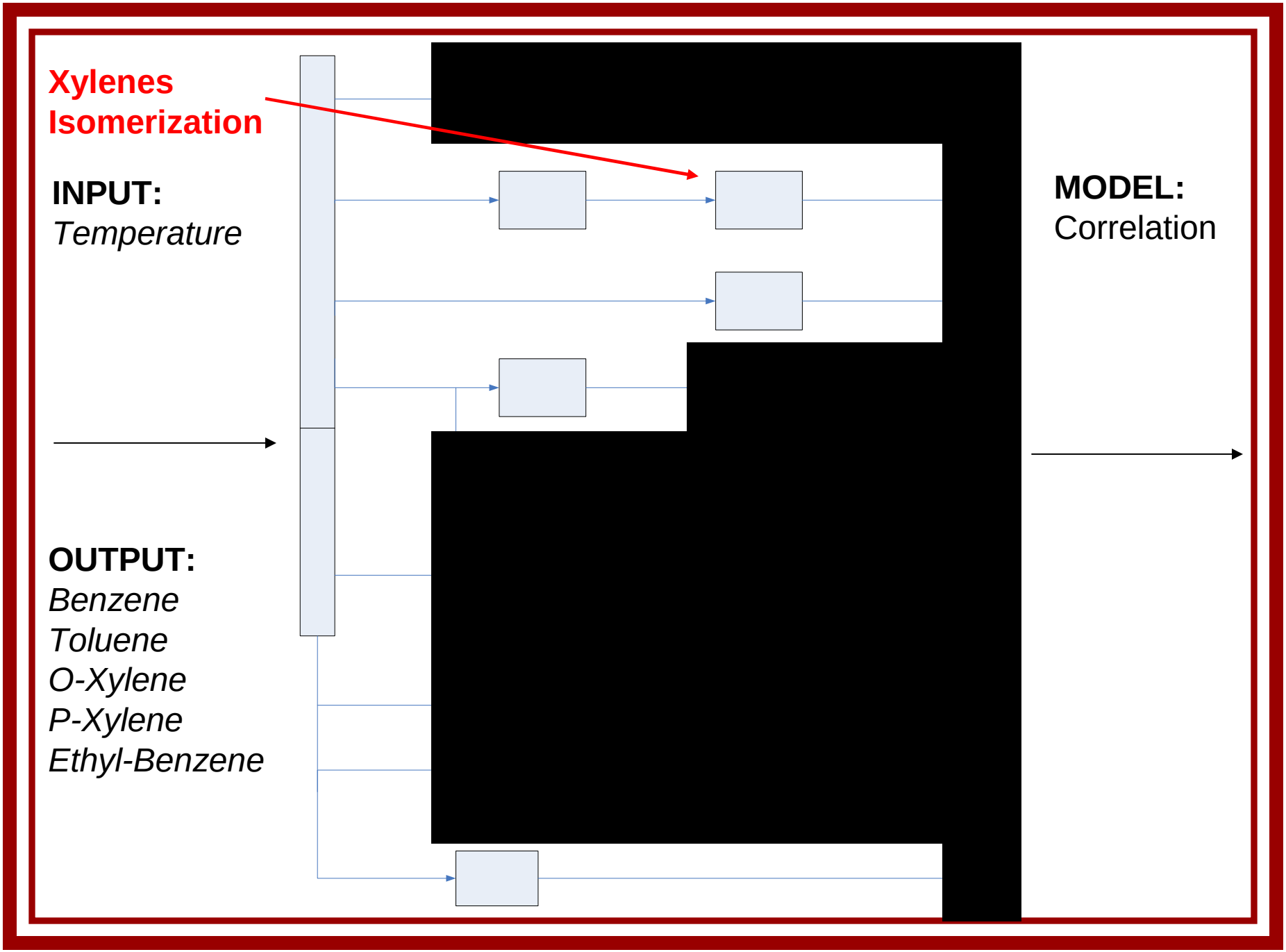
Catalytic Reforming



Catalytic Reforming






Xylenes Isomerization
INPUT:
Temperature
MODEL:
Correlation
OUTPUT:
Benzene
Toluene
O-Xylene
P-Xylene
Ethyl-Benzene

Xylenes Isomerization

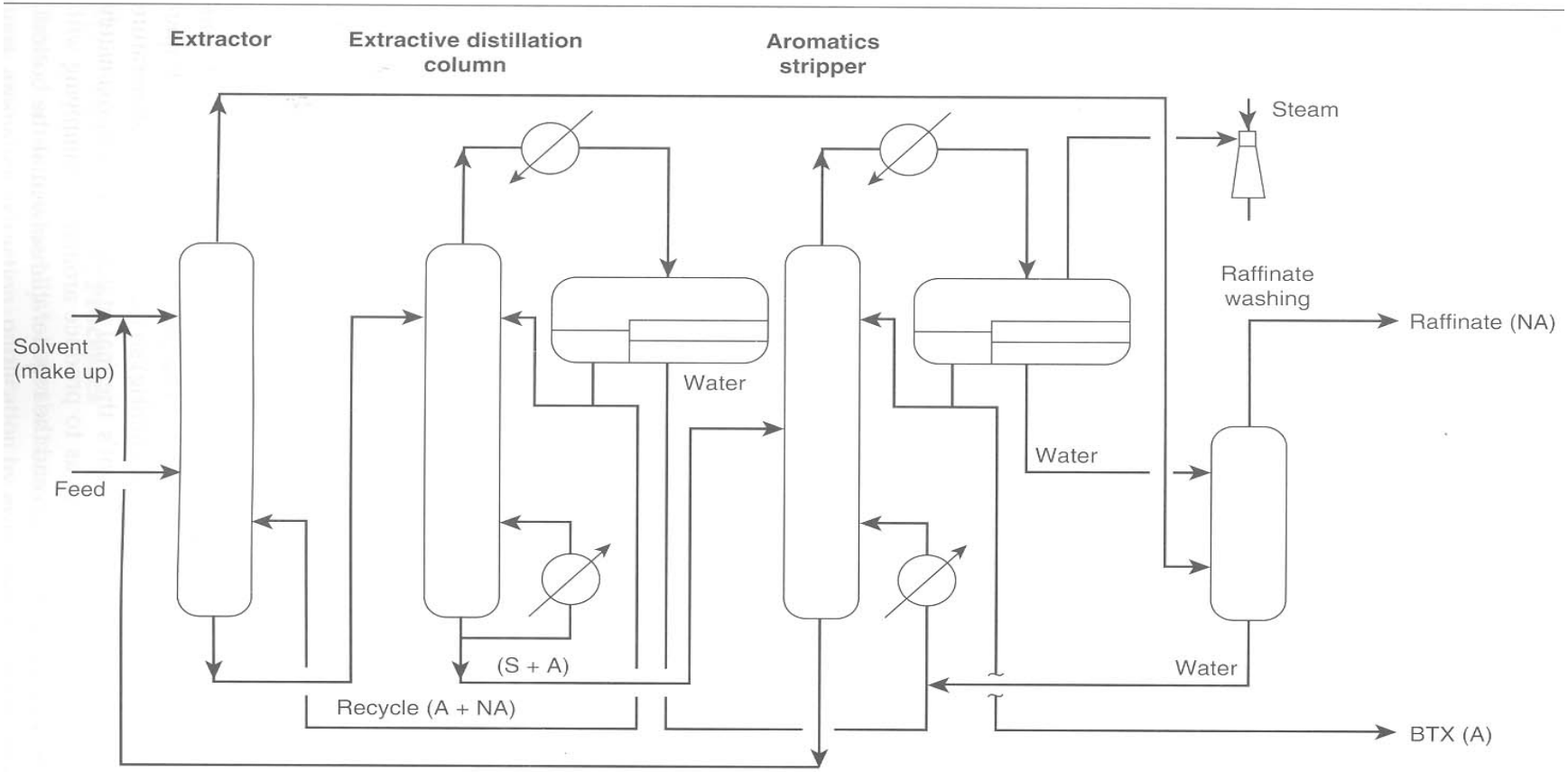
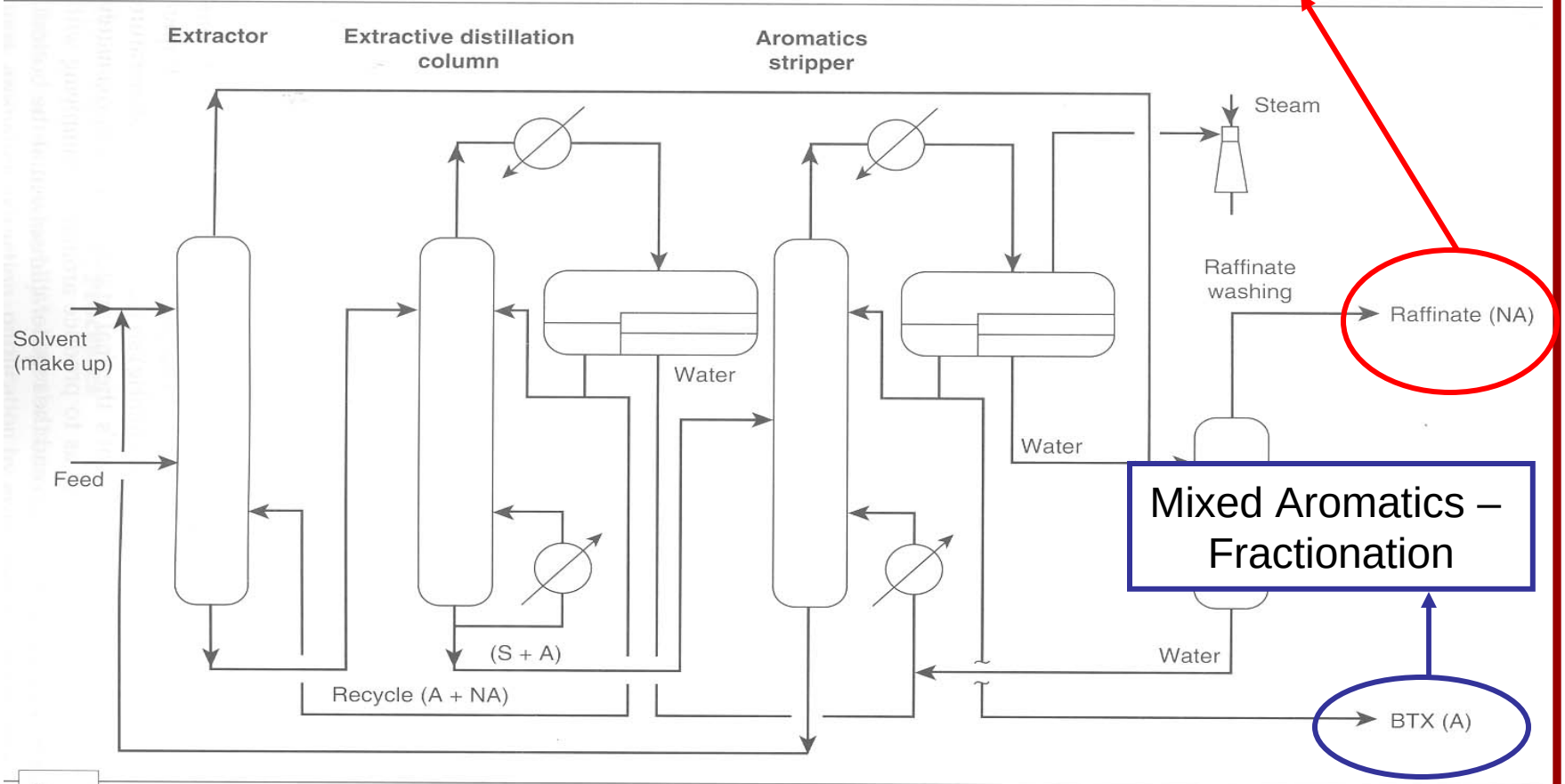


Figure 7.32 *Simplified flow diagram of the Shell/UOP process. S: solvent (sulfolane). A: aromatics. NA: non-aromatics.*

Xylenes Isomerization

Paraffins & Napthenes - Blending



Mixed Aromatics – Fractionation

Figure 7.32 *Simplified flow diagram of the Shell/UOP process. S: solvent (sulfolane). A: aromatics. NA: non-aromatics.*

Xylenes Isomerization

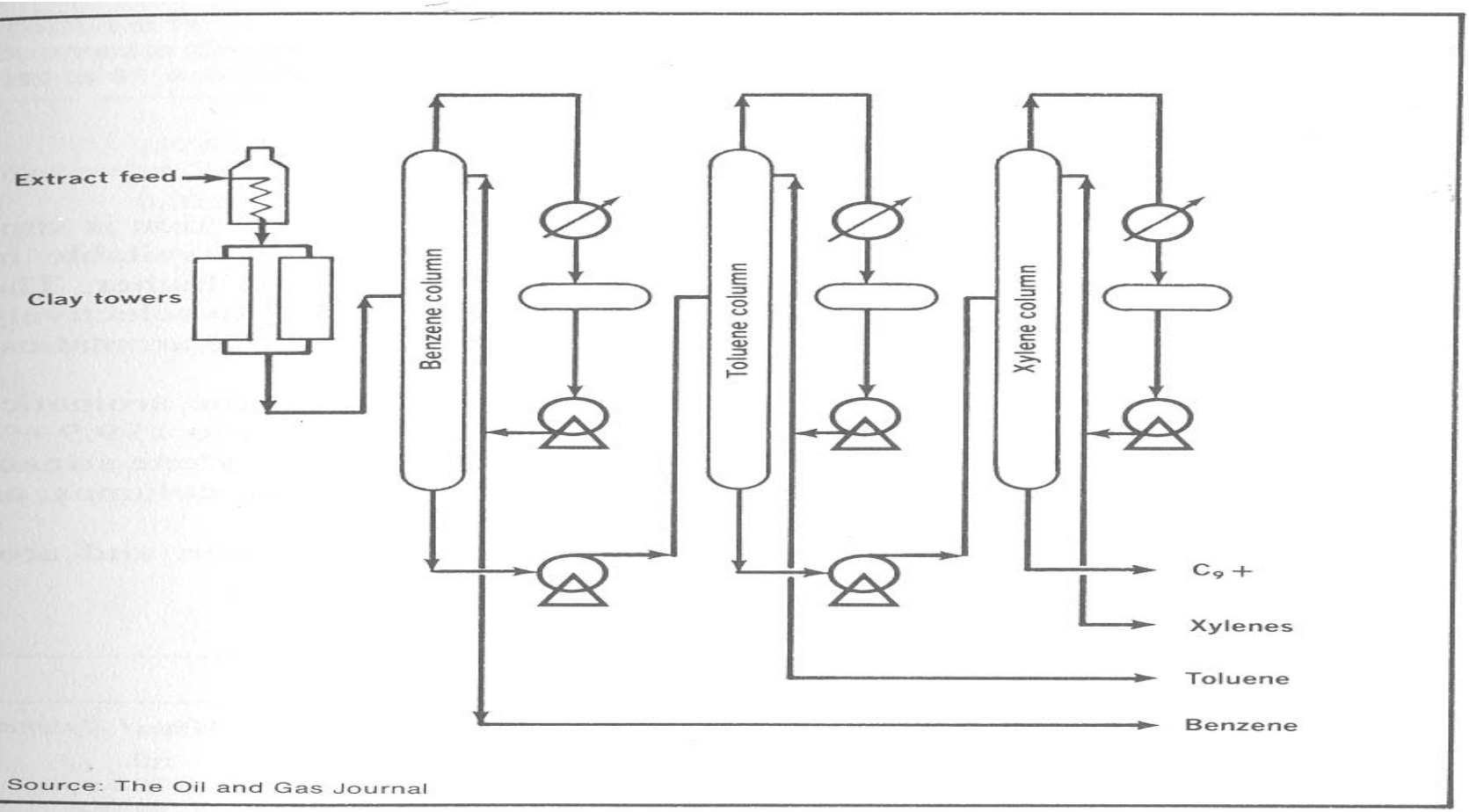


FIG. 2.7 Fractionation of high-purity aromatics

Xylenes Isomerization

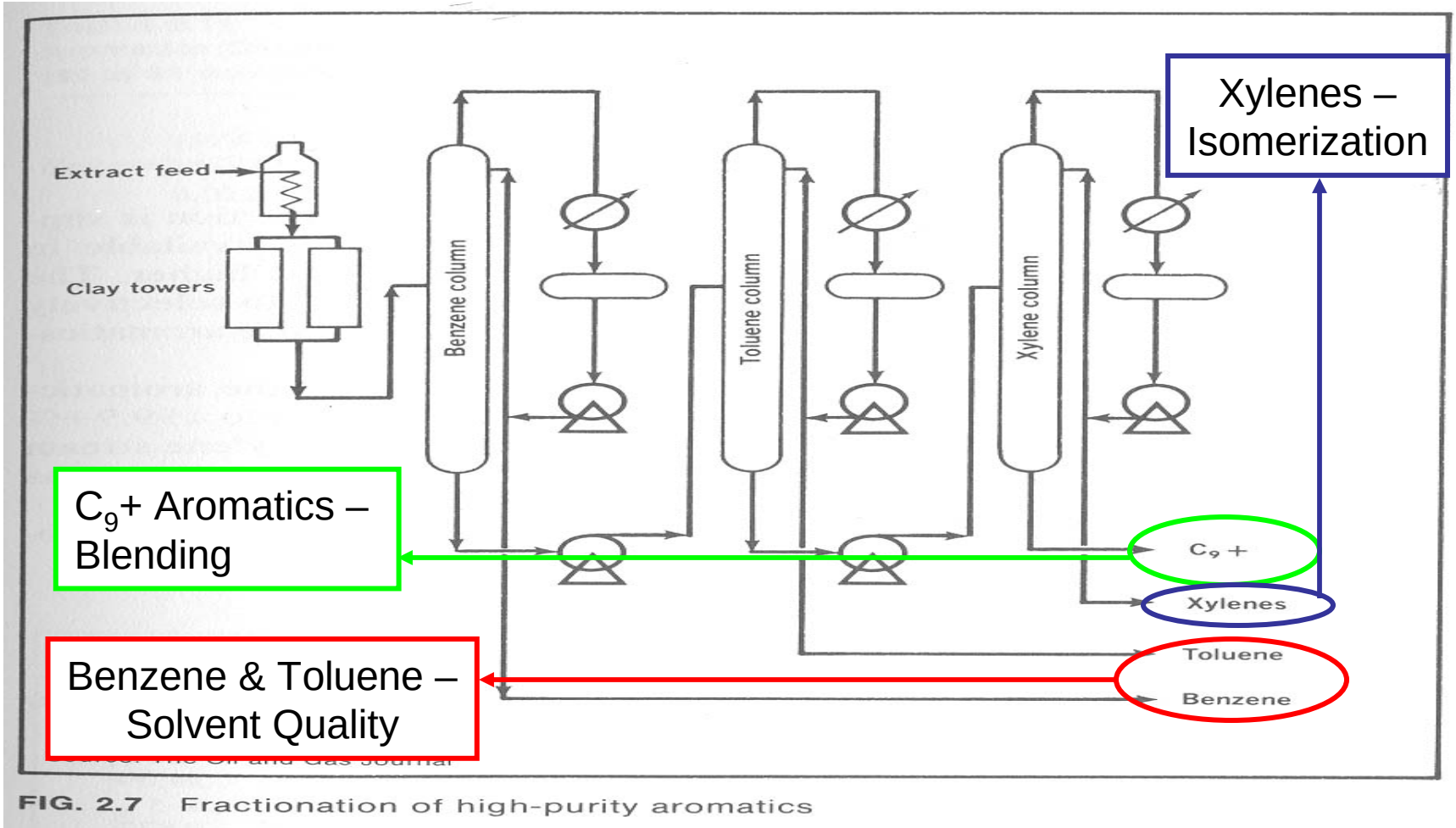


FIG. 2.7 Fractionation of high-purity aromatics

Xylenes Isomerization

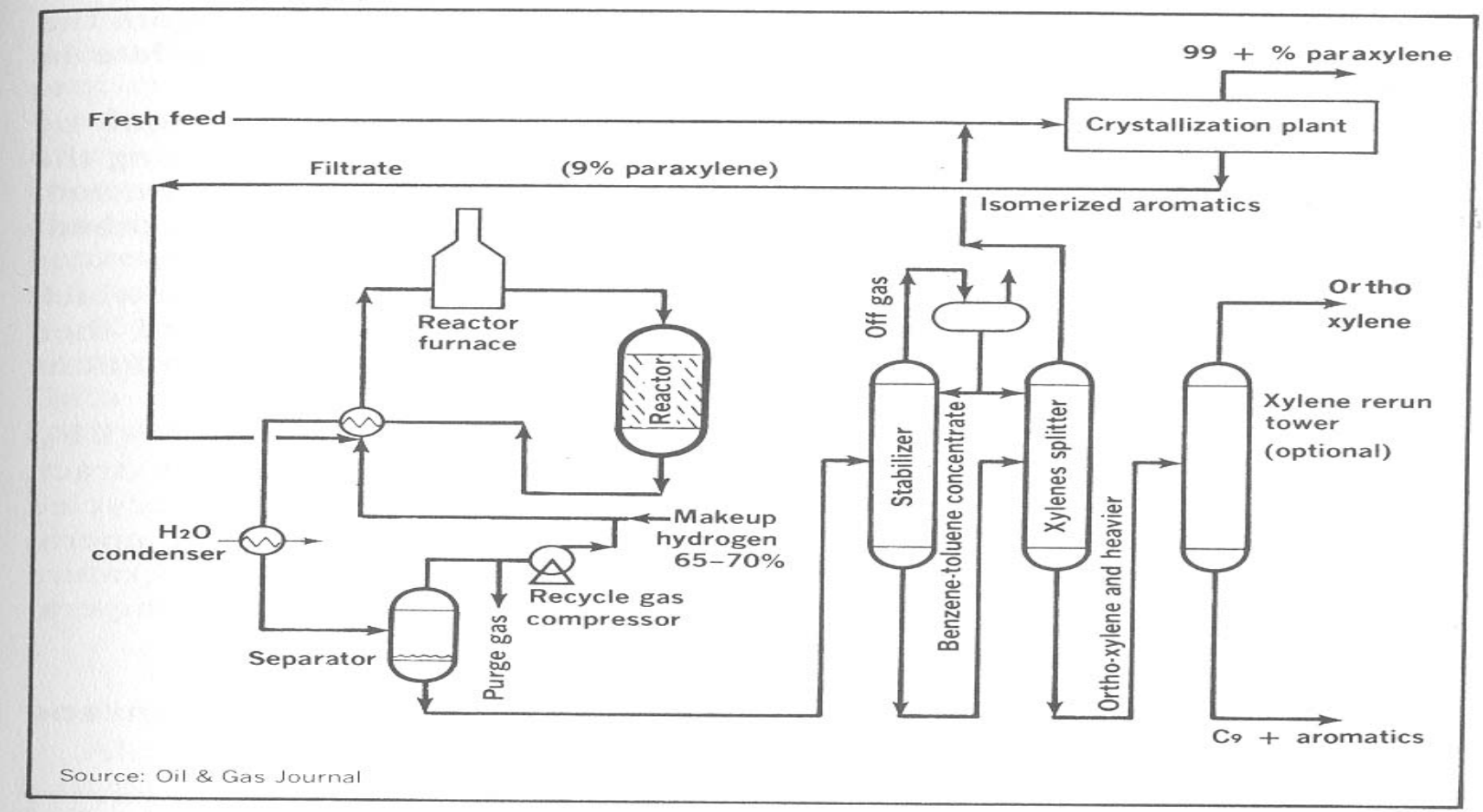


FIG. 2.11 Xylenes processing complex

Xylenes Isomerization

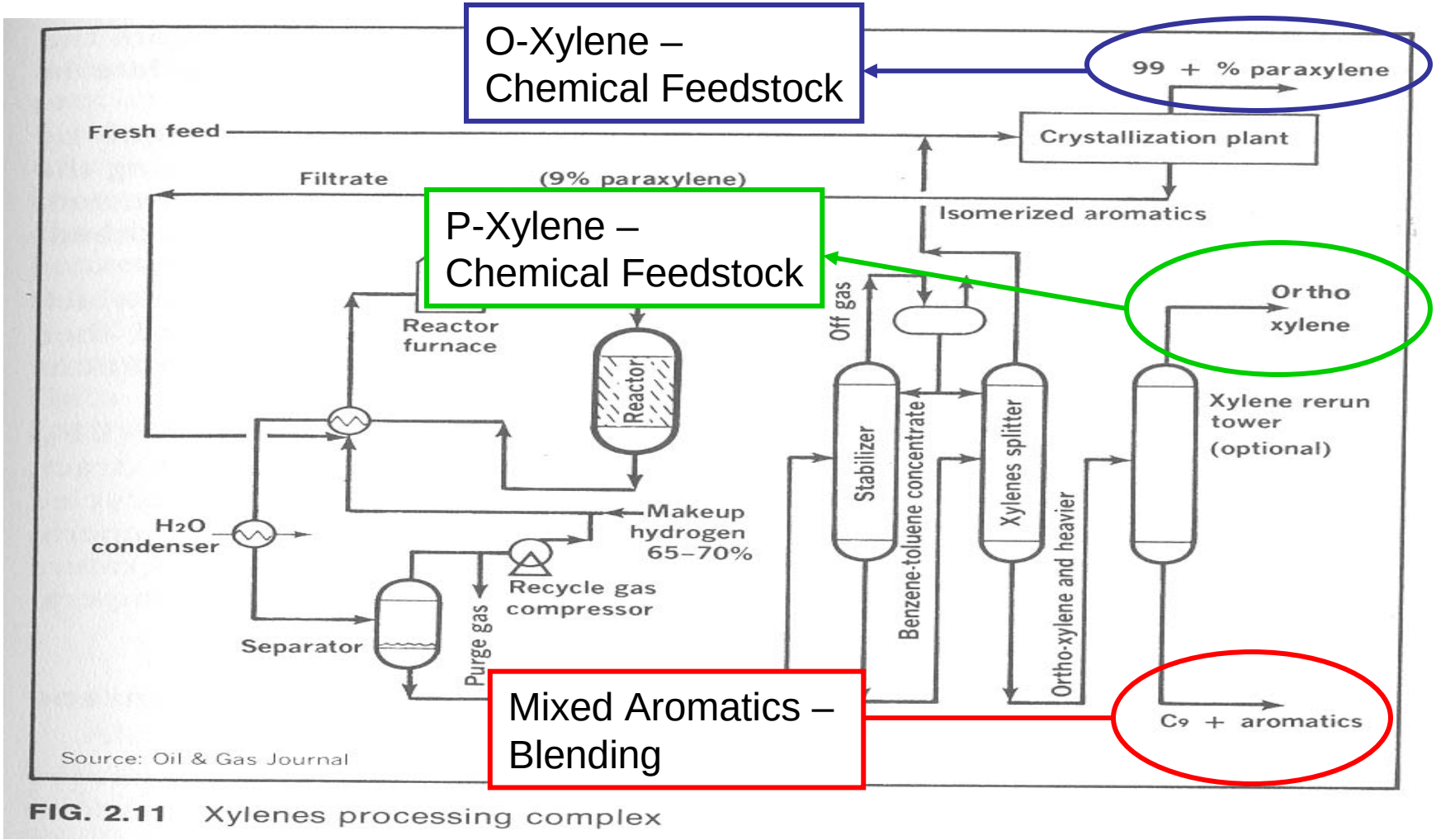


FIG. 2.11 Xylenes processing complex

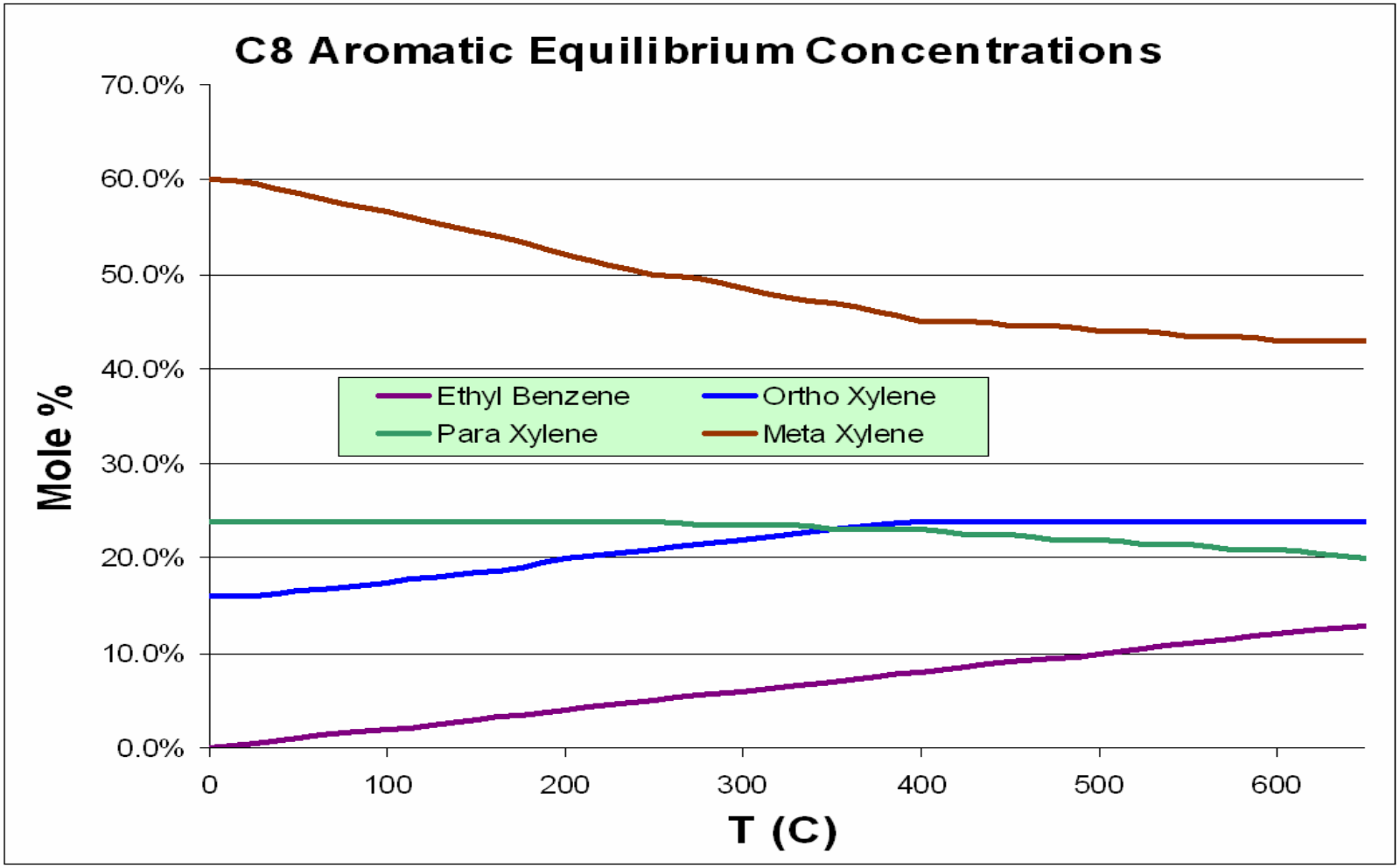
Xylenes Isomerization

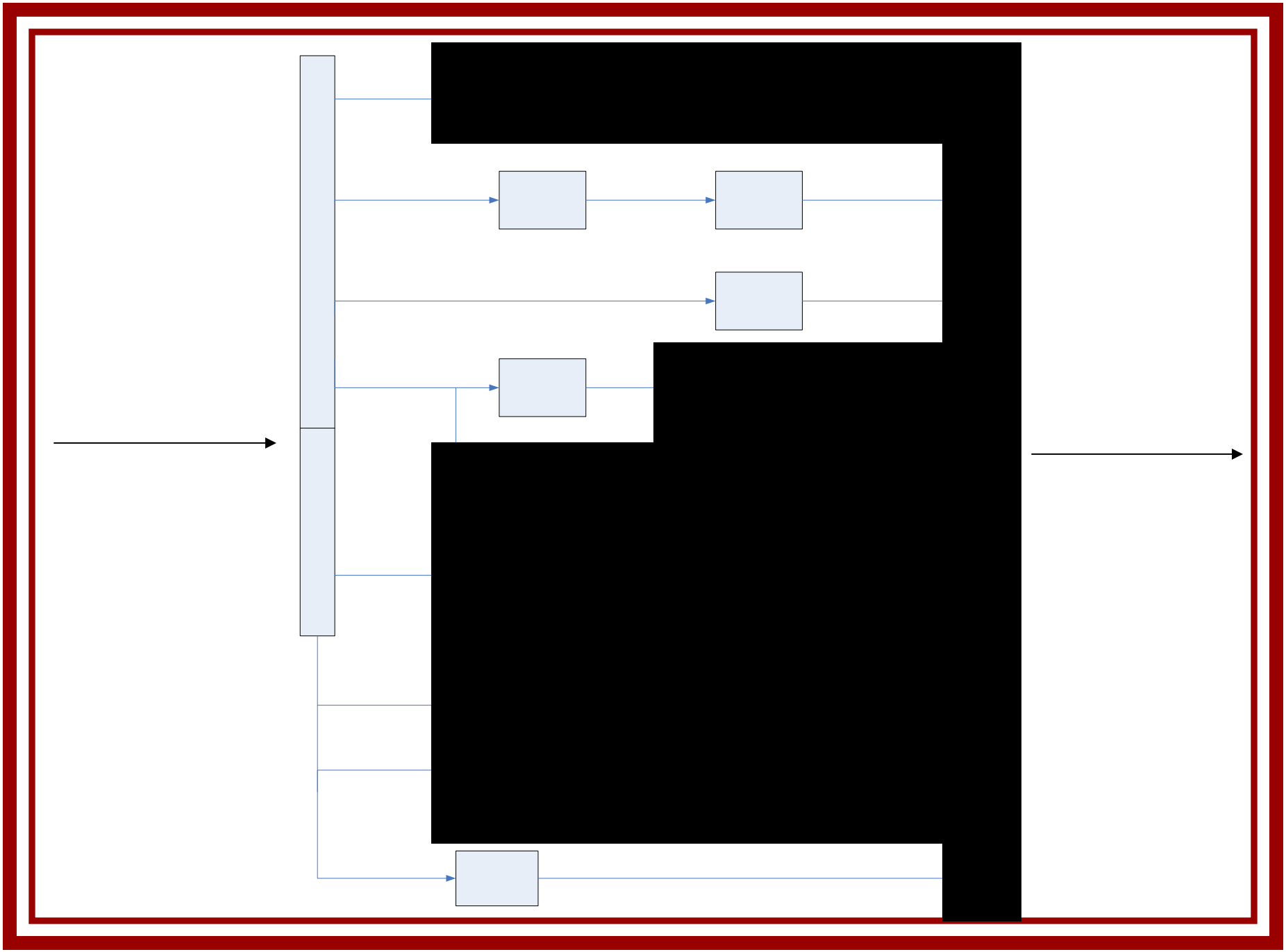
- Reaction driven by equilibrium

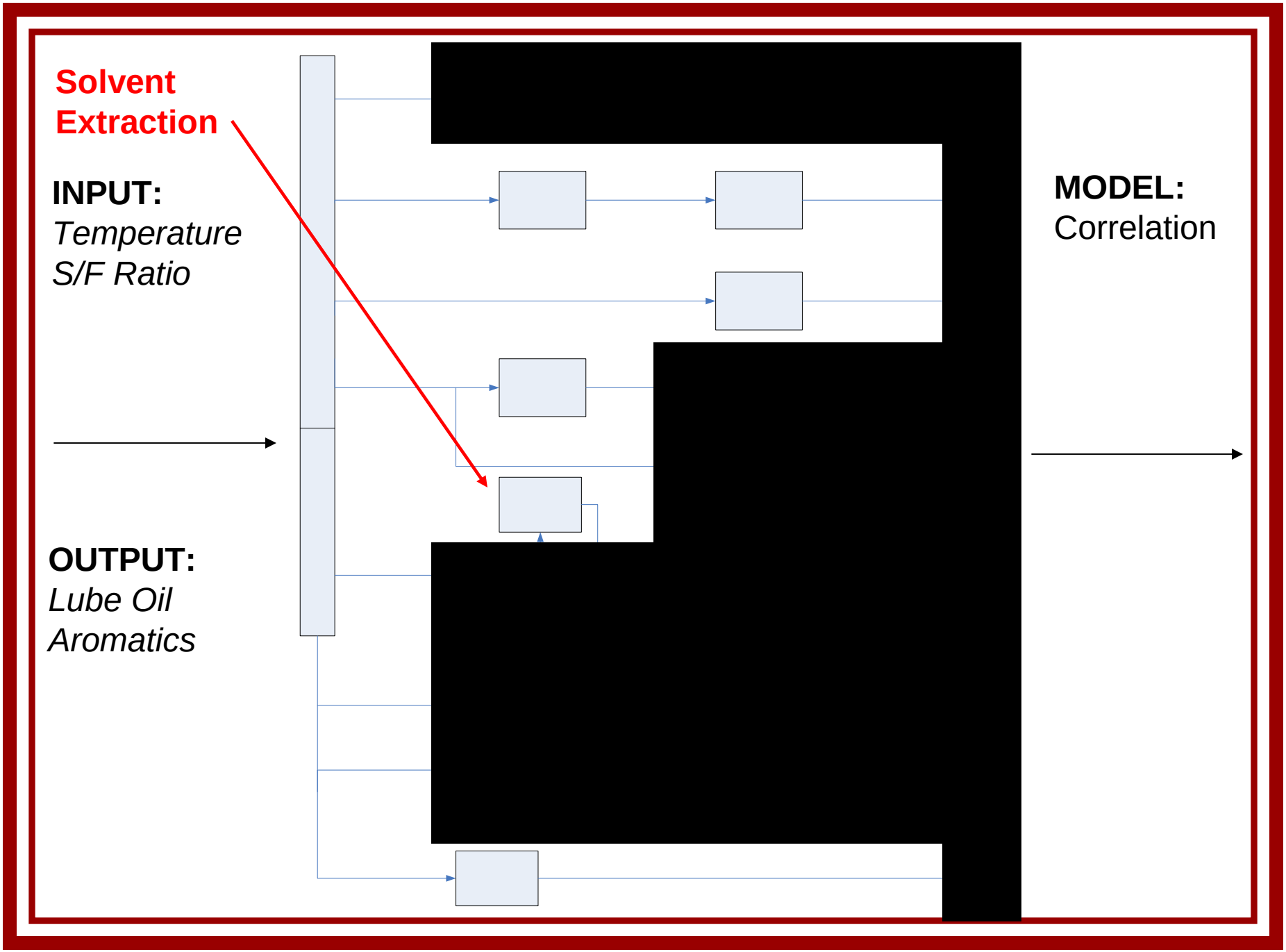
$$m-Xylene \longleftrightarrow o-Xylene \longleftrightarrow p-Xylene \longleftrightarrow EthylBenzene$$

- Temperature dependence of equilibrium modeled in Kirk-Othmer Encyclopedia of Chemical Technology

Xylenes Isomerization






Solvent Extraction
INPUT:
Temperature
S/F Ratio
OUTPUT:
Lube Oil
Aromatics
MODEL:
Correlation

Solvent Extraction

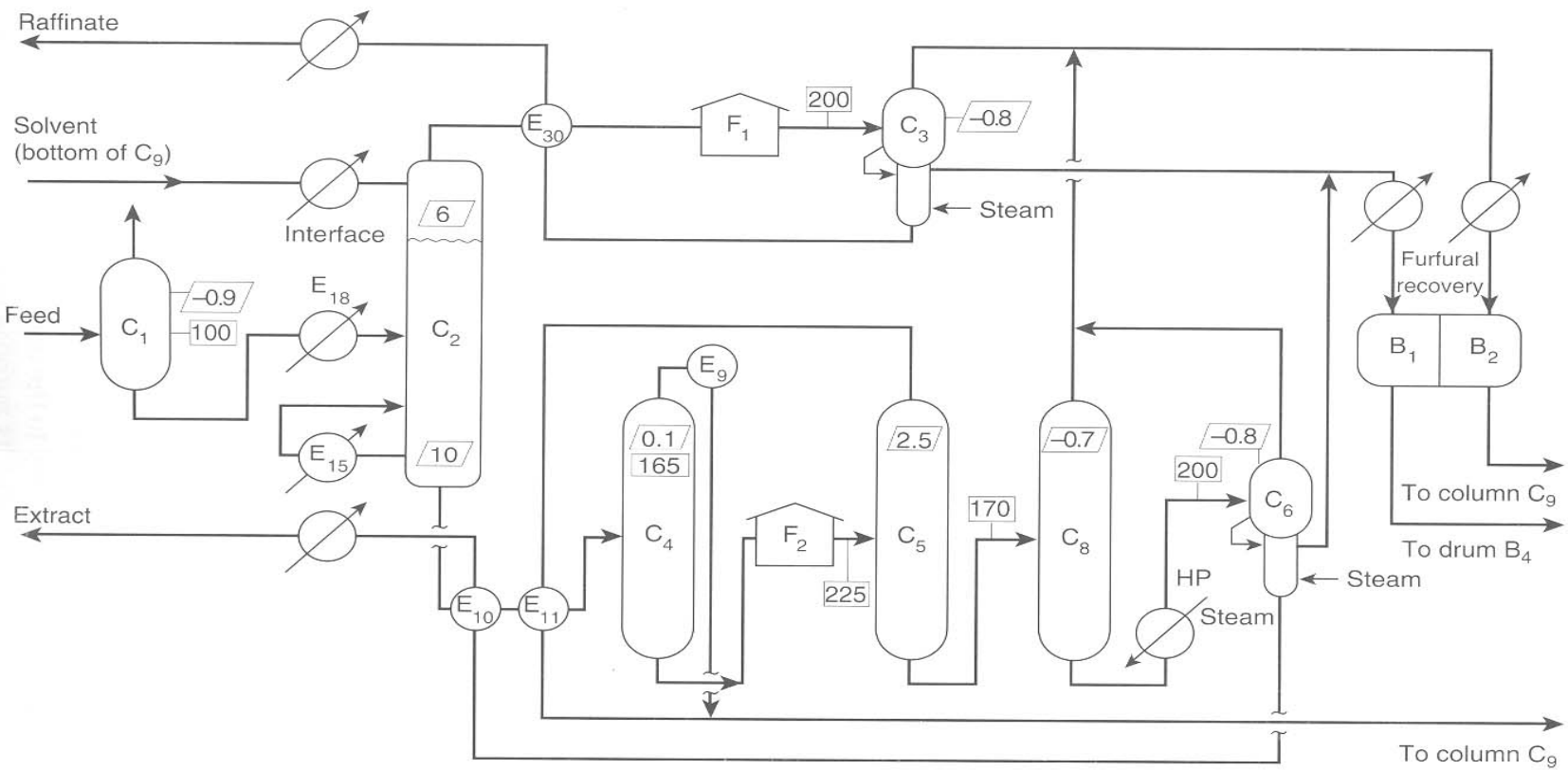
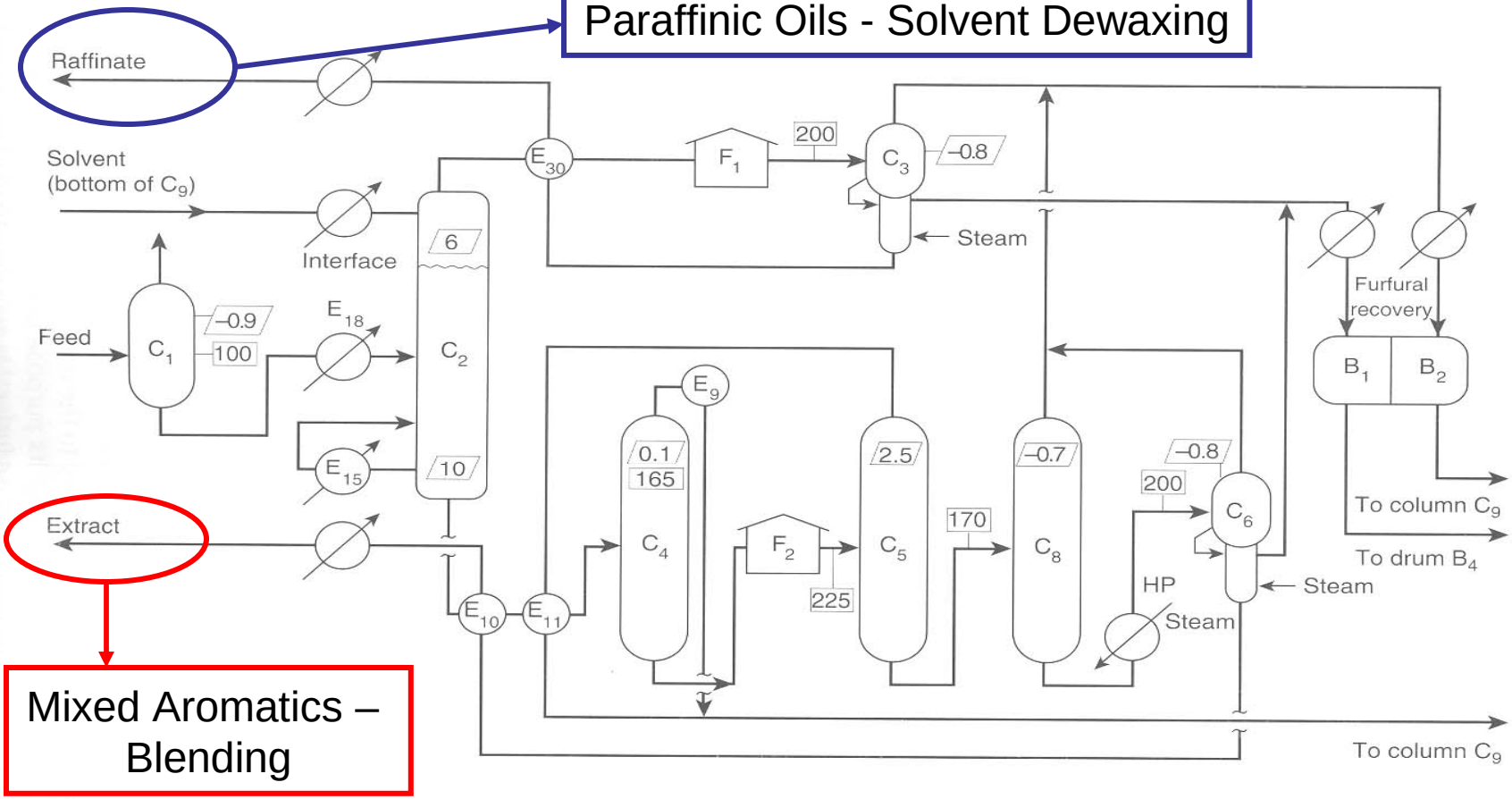


Figure 7.9 *Aromatics extraction unit using furfural. Flow scheme (Source: Mobil).*

Solvent Extraction

Paraffinic Oils - Solvent Dewaxing



Mixed Aromatics – Blending

Figure 7.9 *Aromatics extraction unit using furfural. Flow scheme (Source: Mobil).*

Solvent Extraction

- Furfural Extraction – Averaged K Values
  - Benzene from Cyclohexane
  - Benzene from Iso-octane
  - 1,6-diphenylhexane from Docosane
    - Temperature (ºR) dependence of K correlated from this

$$E = K * \frac{S}{F}$$

$$\%Extracted = 1 - \frac{1}{\sum_{n=0}^{N} E^{n}}$$

$$K = T^{2}\left(-2E5\right) + 0.0259 * T - 7.371$$

Solvent Extraction

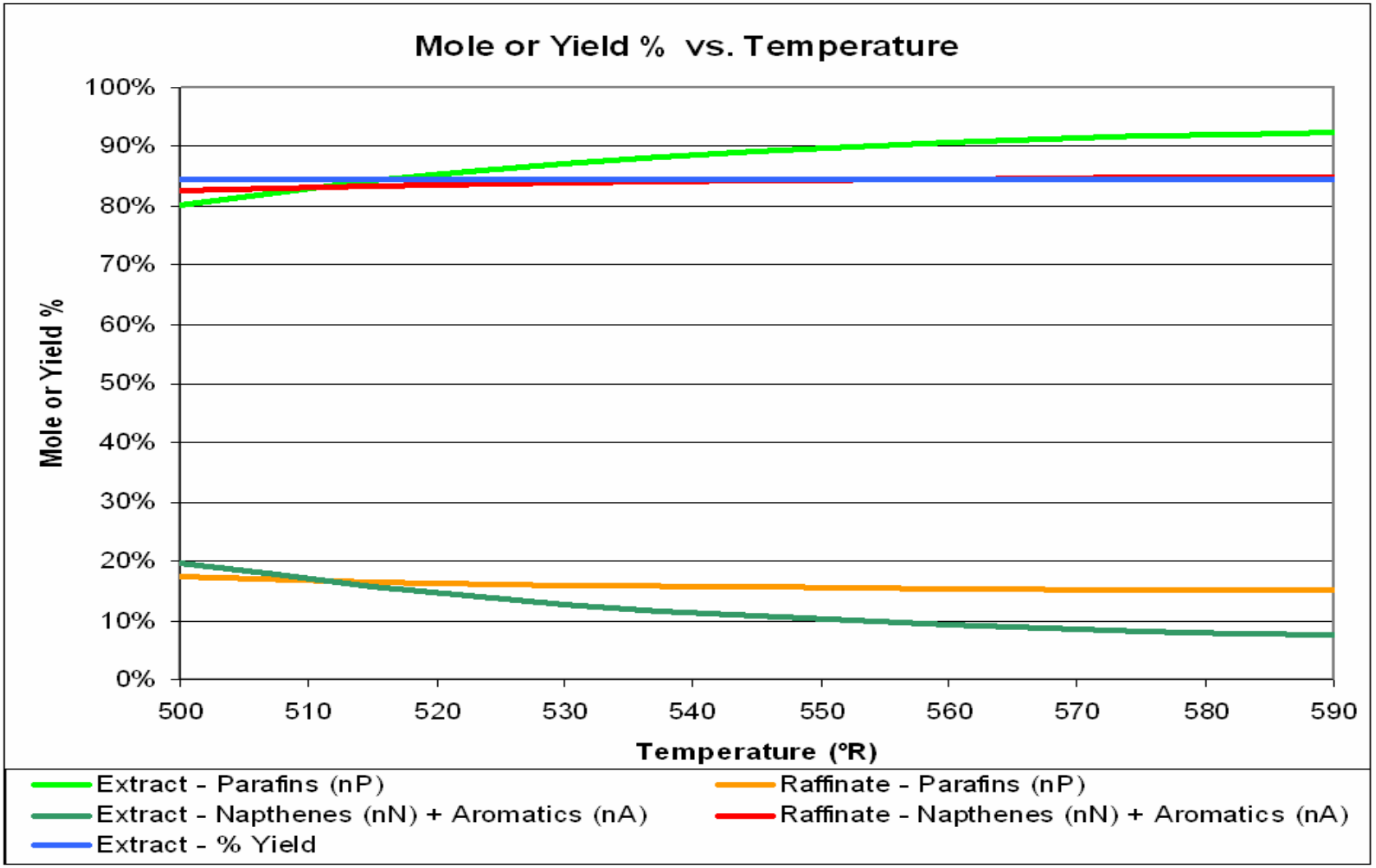
- Correlations developed from Institut Français du Pétrole data

93 wt% Furfual Solvent		
Solvent to Feed Ratio	Raffinate Yield	Raffinate Specific Gravity
0	100%	0.925
3	75%	0.900
6	63%	0.895
9	53%	0.892
12	47%	0.891

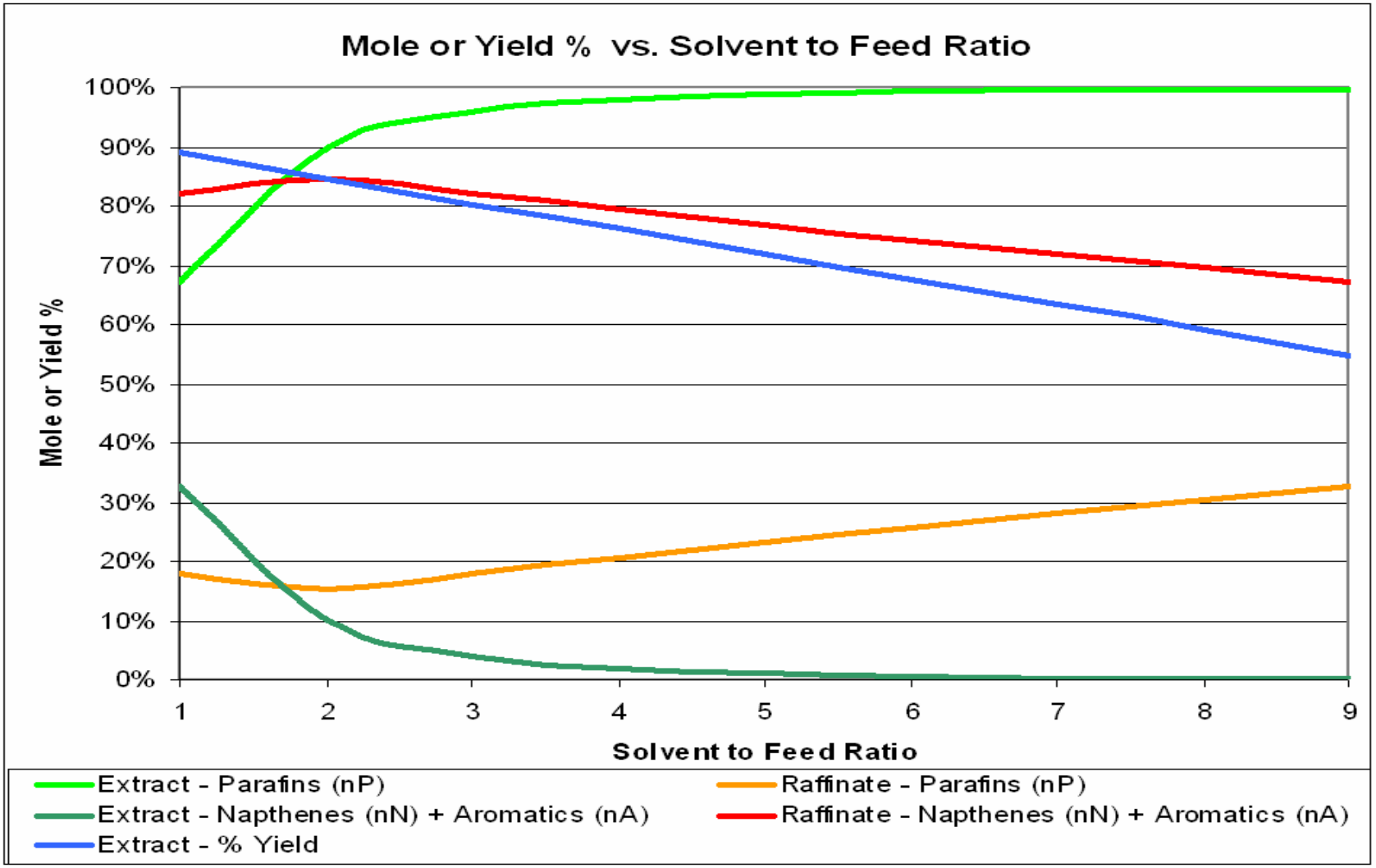
$$RaffinateYield\% = \left(\frac{S}{F}\right) * \left(-0.0426\right) + 0.9318$$

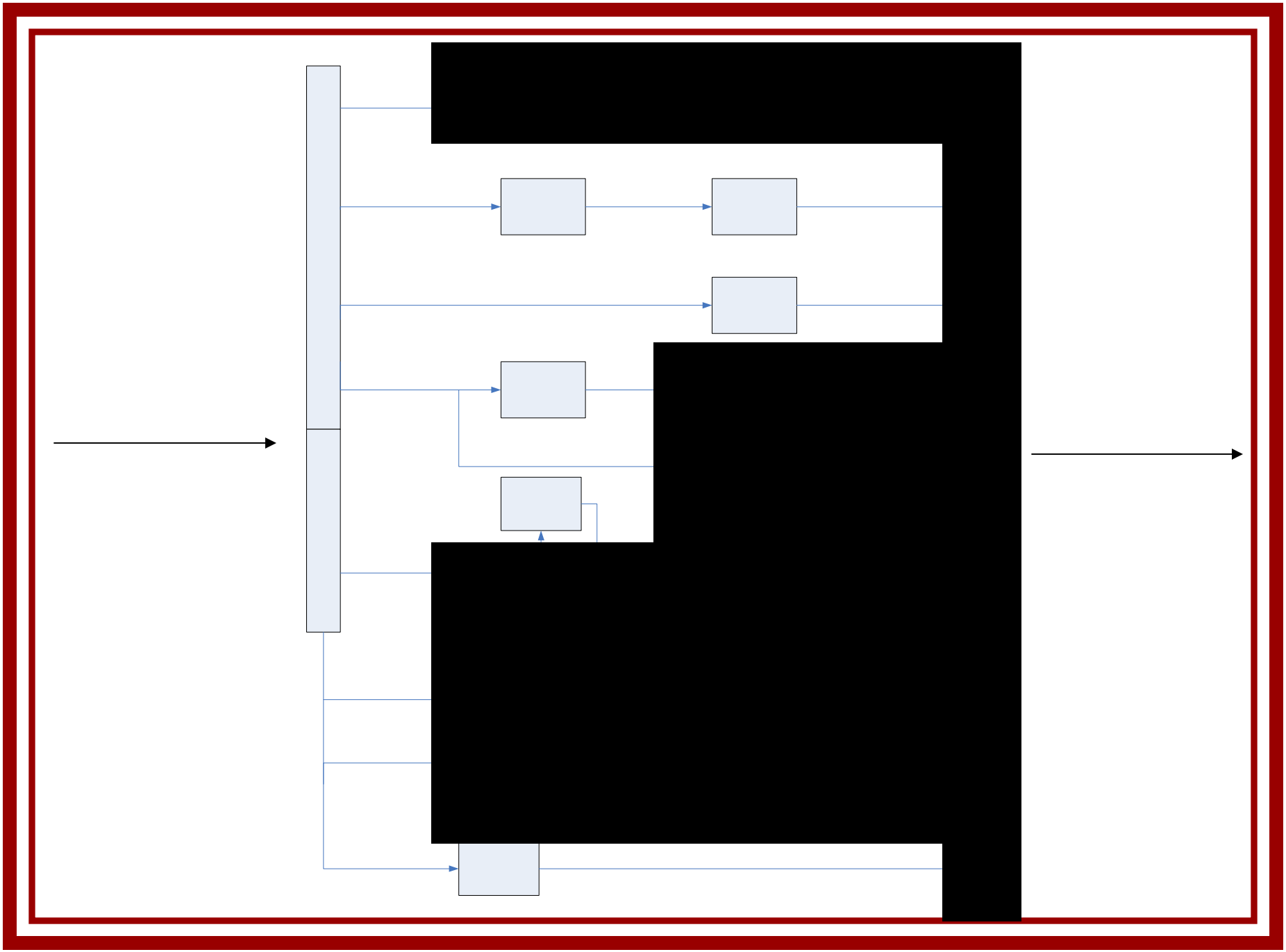
$$RaffinateS.G. = \left(\frac{S}{F}\right)^2 * \left(0.0004\right) - \left(\frac{S}{F}\right) * \left(0.0073\right) + 0.9229$$

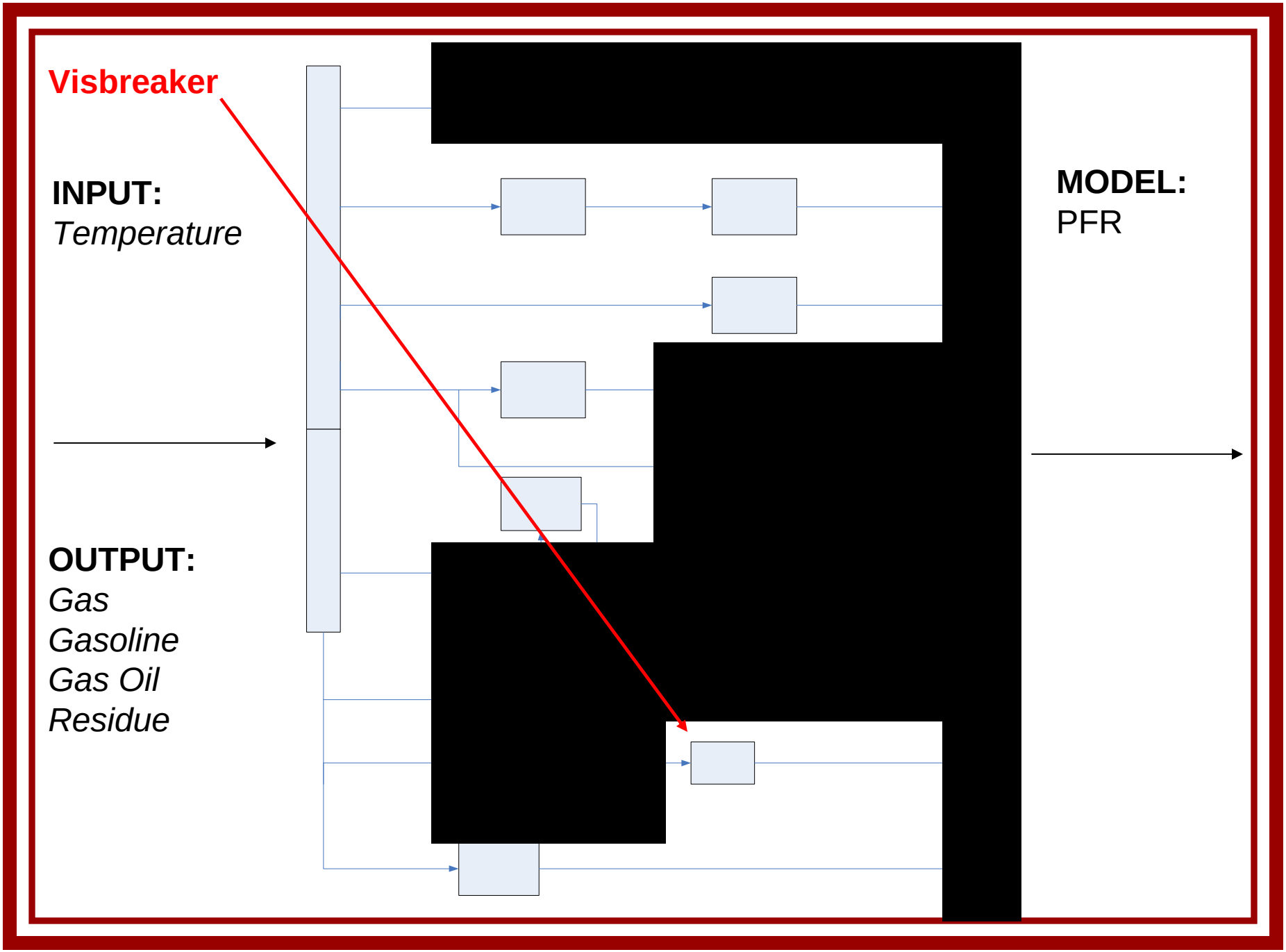
Solvent Extraction



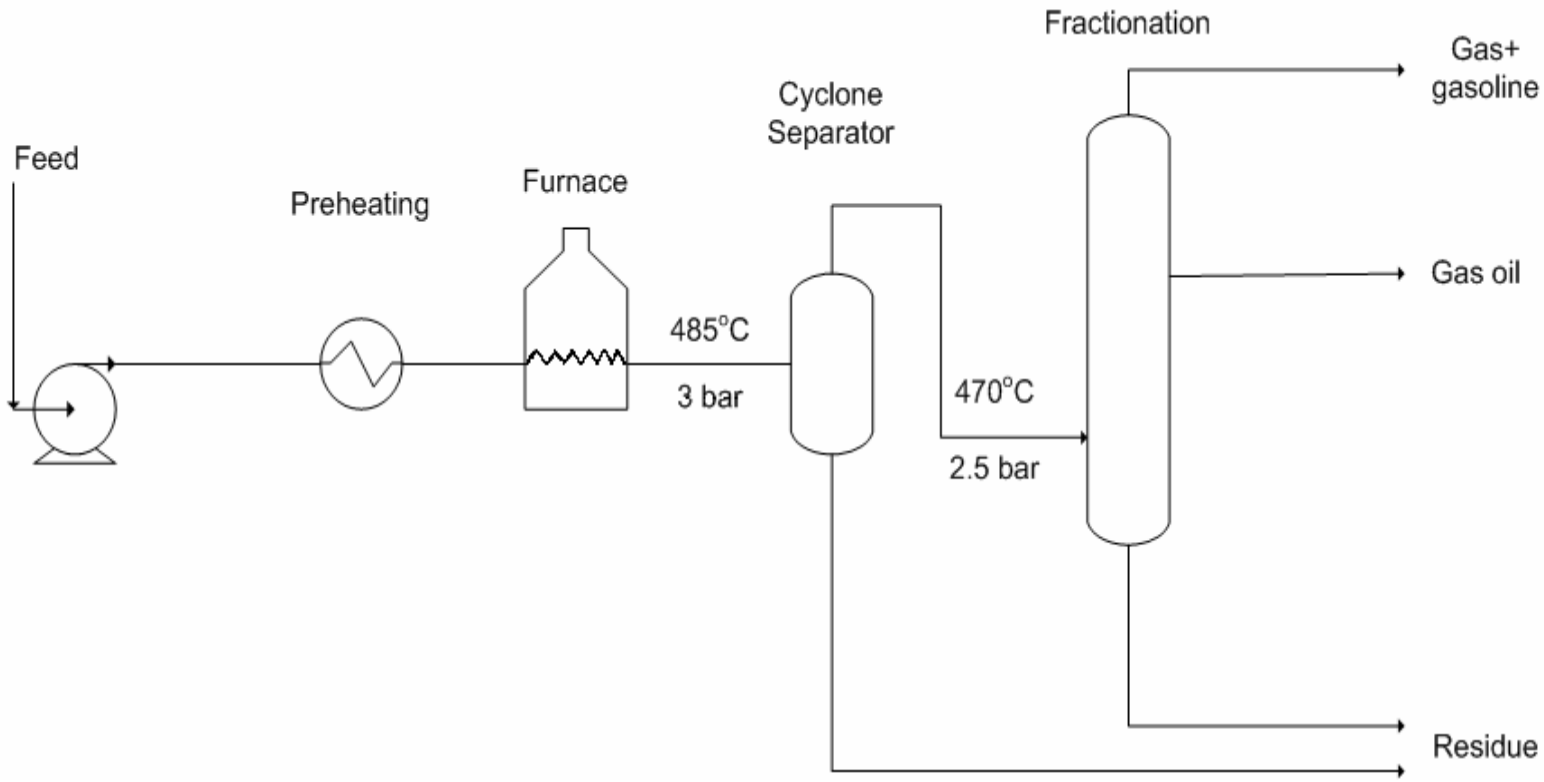
Solvent Extraction






Visbreaker
INPUT:
Temperature
MODEL:
PFR
OUTPUT:
Gas
Gasoline
Gas Oil
Residue

Visbreaking

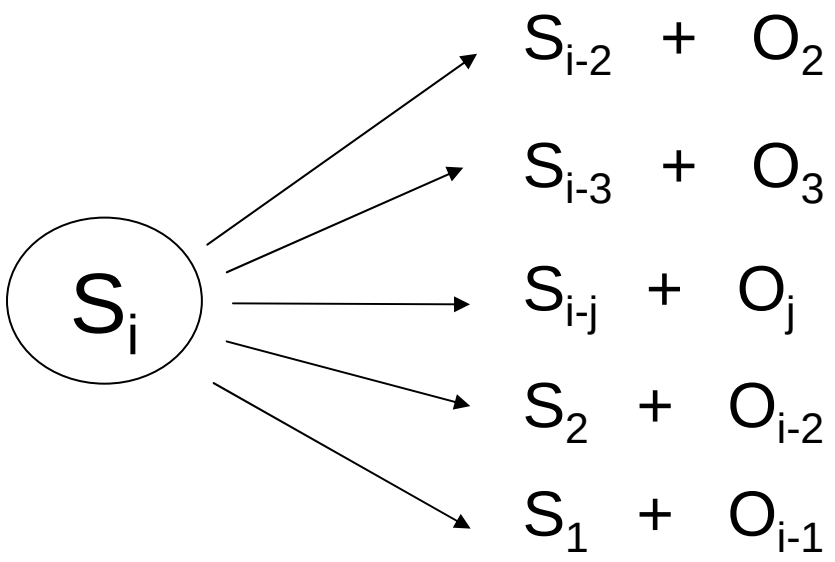


Visbreaking

- Carbon chains cracking into smaller chains of varying carbon numbers

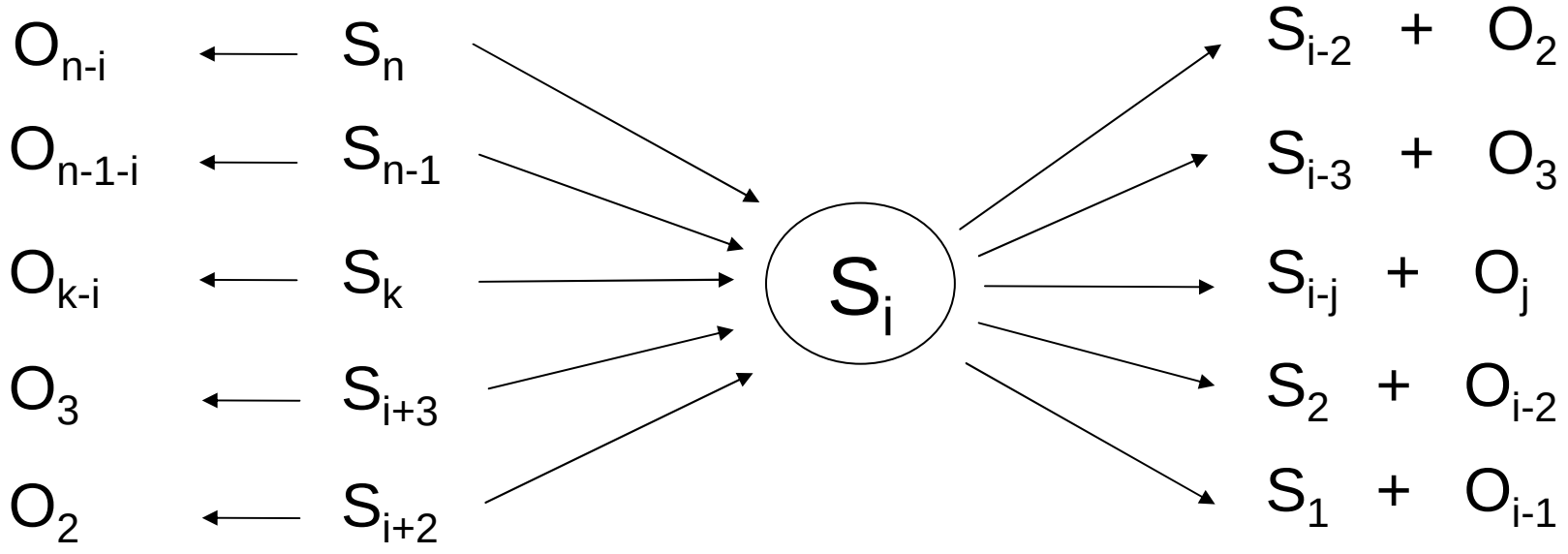
Visbreaking

- S_i forms all components with carbons less than i-1



Visbreaking

- S_i forms all components with carbons less than i-1
- S_i is formed from all components with carbons greater than i+1



Visbreaking

- First order kinetics with molar concentrations

$$rs_i = \sum_{k=i+2}^{n} K_{k,i} Cs_k - Cs_i \sum_{j=1}^{i-2} K_{i,j}$$

$$ro_i = \sum_{j=i+1}^{n} K_{j,j-i} Cs_j$$

$$\frac{dCs_i}{dz} = \frac{1}{4}\pi\phi^2 \frac{\rho}{F} rs_i$$

$$\frac{dCo_i}{dz} = \frac{1}{4}\pi\phi^2 \frac{\rho}{F} ro_i$$

Visbreaking

- Rate Constant dependent on molecular weight

$$K_{i,j} = A_{i,j} e^{-B_{i,j}/RT}$$

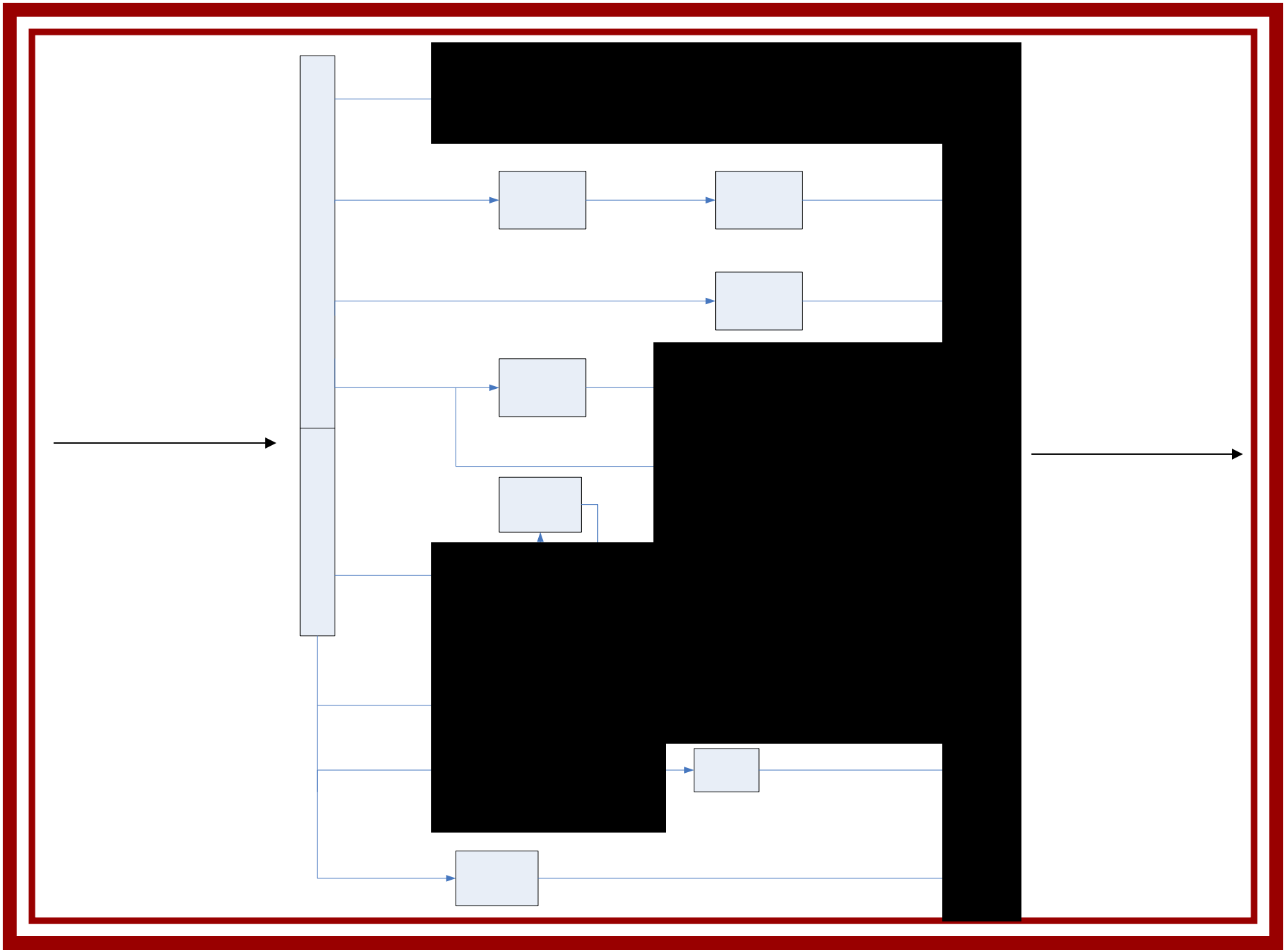
$$B_{i,j} = b_0 + b_1 \cdot PM_i + b_2 \cdot PM_j$$

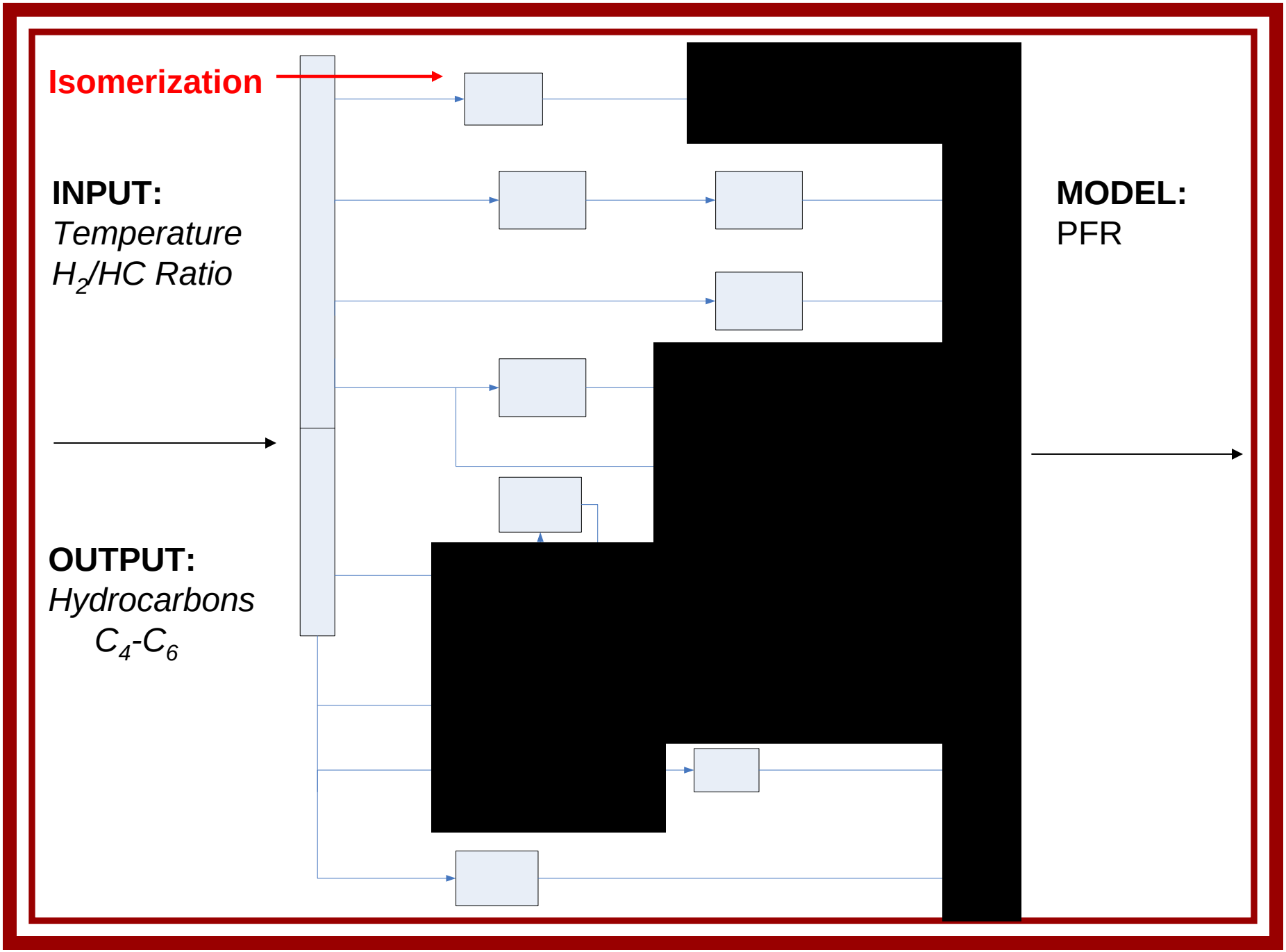
$$A_{i,j} = \left(a_0 + a_1 \cdot PM_i + a_2 \cdot [PM_i]^2\right) e^{-\frac{1}{2}\left(\frac{PM_j - \frac{PM_i}{a_4}}{a_3}\right)^2}$$

a	b
1.51E+12	42894
1.90E+08	-4.5
2.06E+06	3
146.95	
11.35	

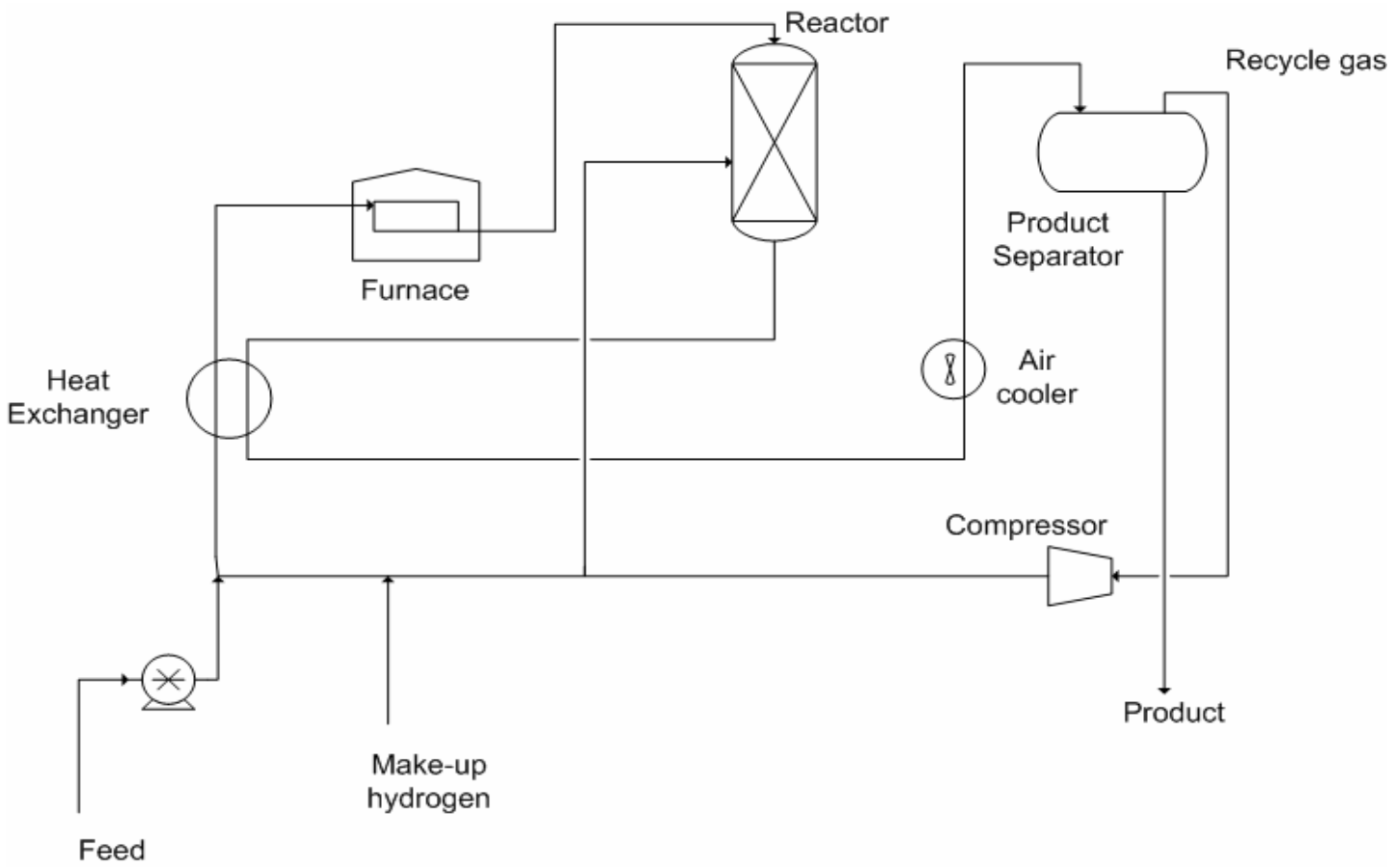
Visbreaking

- Model inputs
  - Temperature and mass flow rate
- Model Product form
  - Weight percents
  - Components are lumped into 4 categories
    - Gas: C1-C4
    - Gasoline: C5-C10
    - Gas Oil: C11-C21
    - Residue: C22-C45



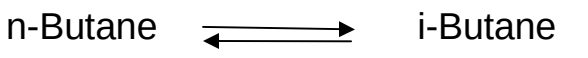

Isomerization
INPUT:
Temperature
H2/HC Ratio
MODEL:
PFR
OUTPUT:
Hydrocarbons
C4-C6

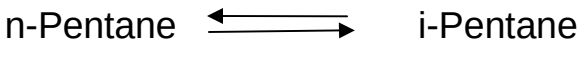
Isomerization

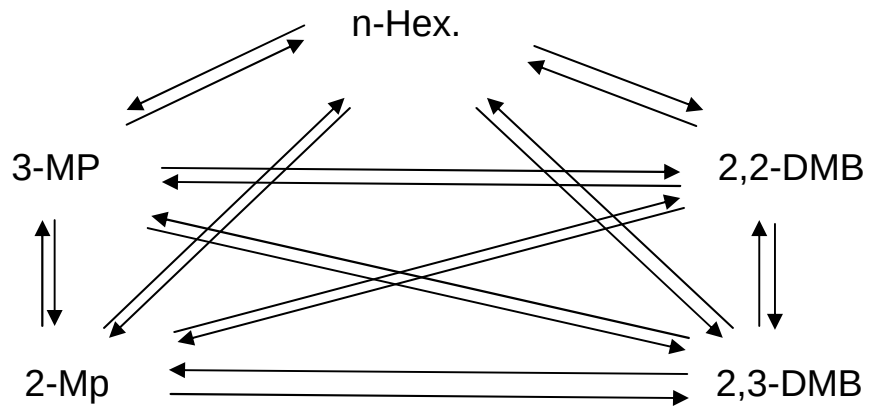


Isomerization

- Main reactants: n-Butane, n-Pentane, n-Hexane
- Typically catalyzed-gas phase reaction
- Low temperature favors isomer formation
- Seven rate laws
  - Only one of n-Pentanes isomers forms







Isomerization

- n-Butane

$$r_{n-C4} = -K_1 \cdot \frac{P_{n-C_4}}{P_{H_2}} + K_2 \cdot \frac{P_{iso-C_4}}{P_{H_2}}$$

- n-Pentane

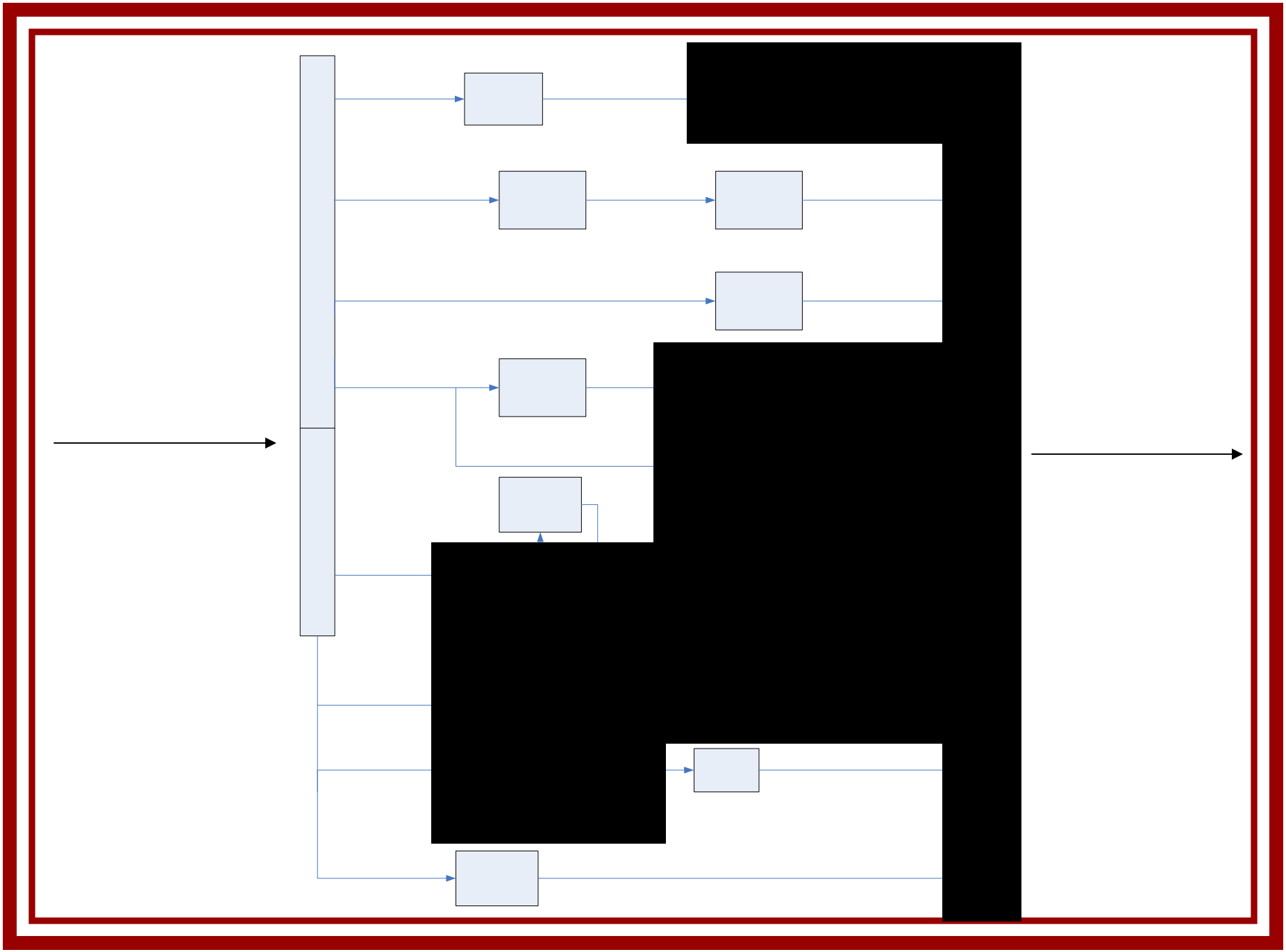
$$r_{n-C5} = -\left[K_2 \cdot \left(\frac{C_{n-C5}}{[H_2]} \right)^{0.125} - 0.0000197 \cdot t \right] \left[K_{eq} \cdot C_{n-C5} - (K_{eq} + 1) \cdot C_{i-C5} \right]$$

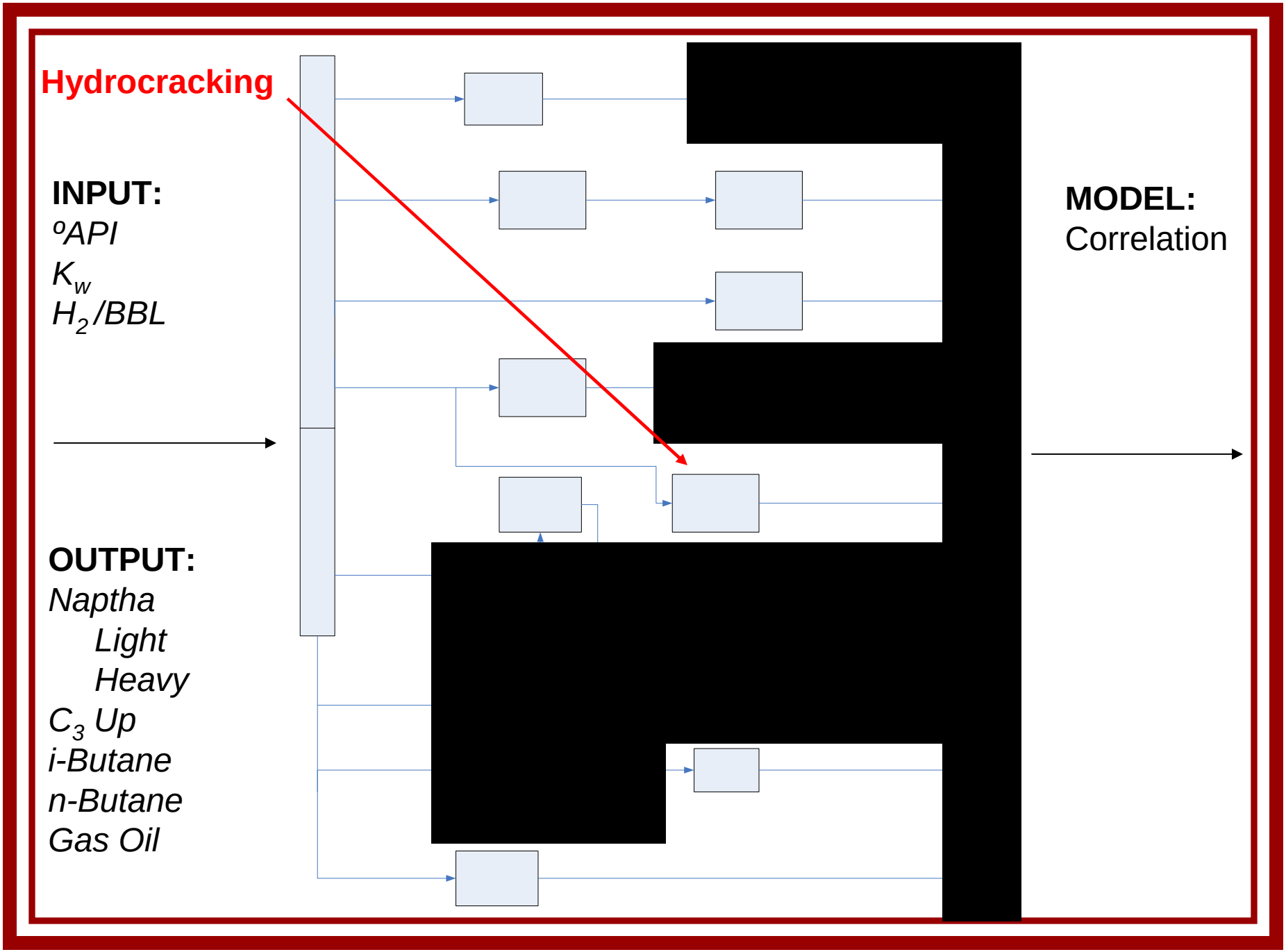
- n-Hexane

$$r_i = -\left(\sum_{j=1}^{5} K_{j,i} \right) \cdot C_i + \sum_{j=1}^{5} K_{i,j} C_j$$

Isomerization

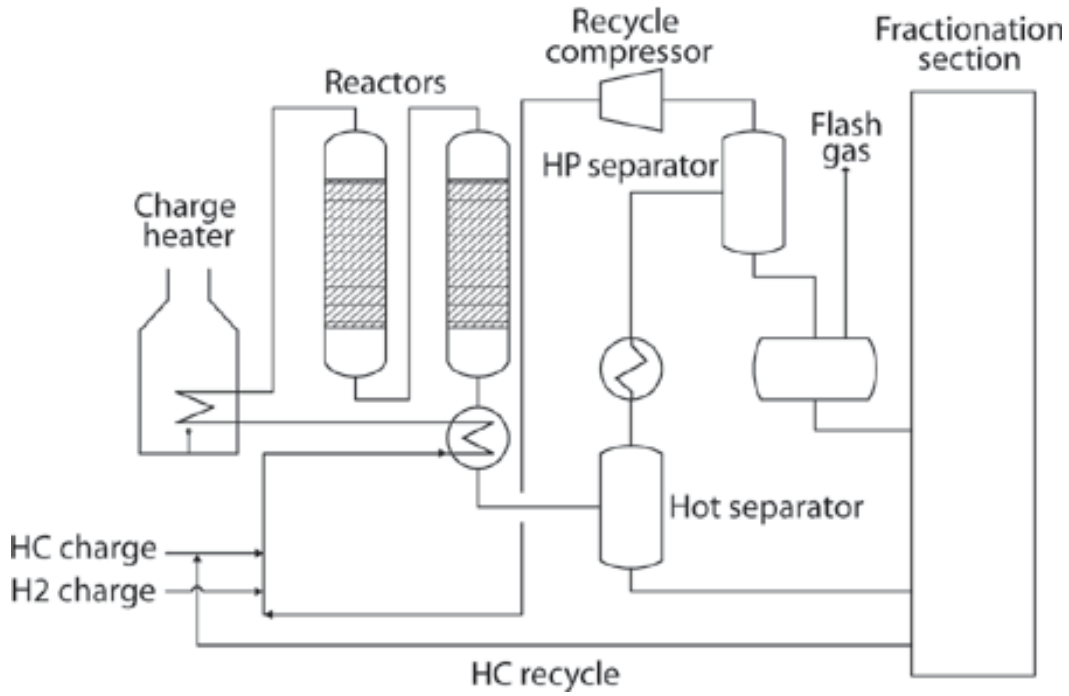
- Model inputs
  - Temperature, mass flow rate, and H_2/HC ratio
- Model Product form
  - Weight percents of the individual isomers




Hydrocracking
INPUT:
ºAPI
K_w
H_2/BBL
OUTPUT:
Naptha
Light
Heavy
C_3 Up
i-Butane
n-Butane
Gas Oil
MODEL:
Correlation

Hydrocracking

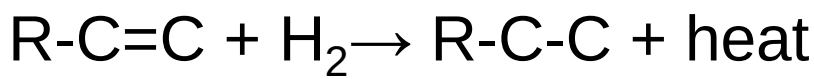
- Convert higher boiling point petroleum fractions into lighter fuel products



Hydrocracking

- Complementary Reactions
  - Cracking reactions
    - Provides olefins for hydrogenation

  - Hydrogenation reactions
    - Provides heat for cracking



Hydrocracking

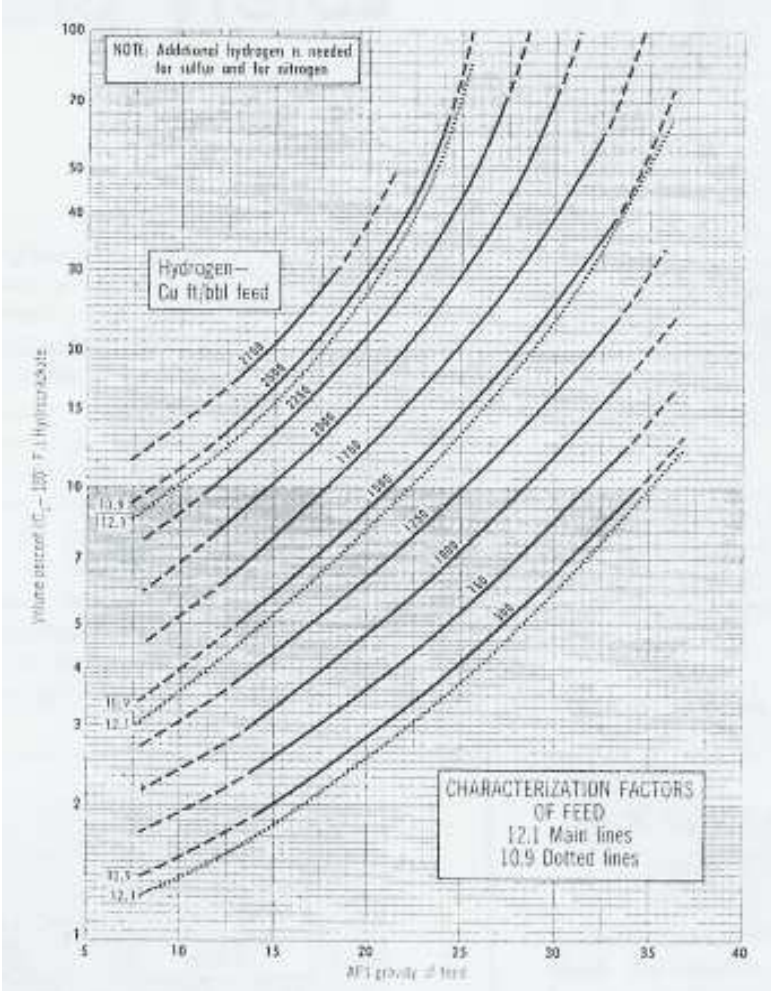
- Feedstocks- Heavy distillate stocks, aromatics, cycle oils, and coker oils
- Catalysts- zeolites
- Operating conditions-

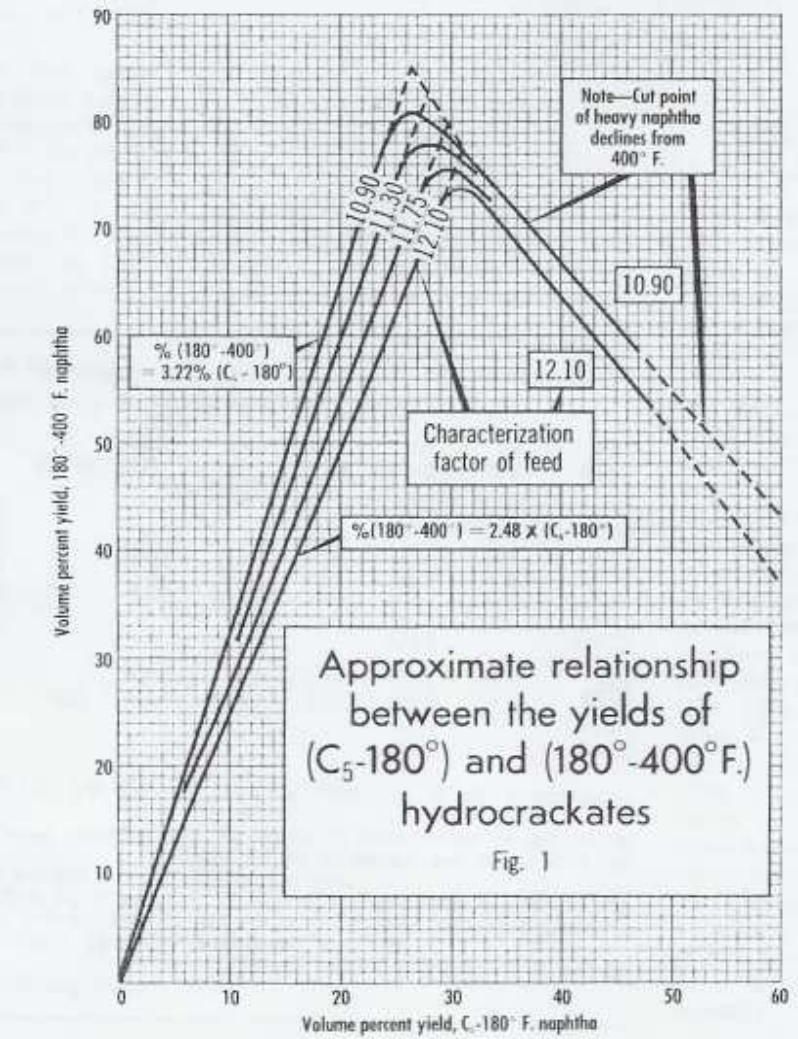
	Residuum	Distillate
Hydrogen Consumption (SCFB)	1200-1600	1000-2400
LHSV (hr^{-1})	0.2-1	0.5-10
Temperature (℉)	750 -800	500-900
Pressure (psi)	2000-3000	500-3000

Hydrocracking Model Development

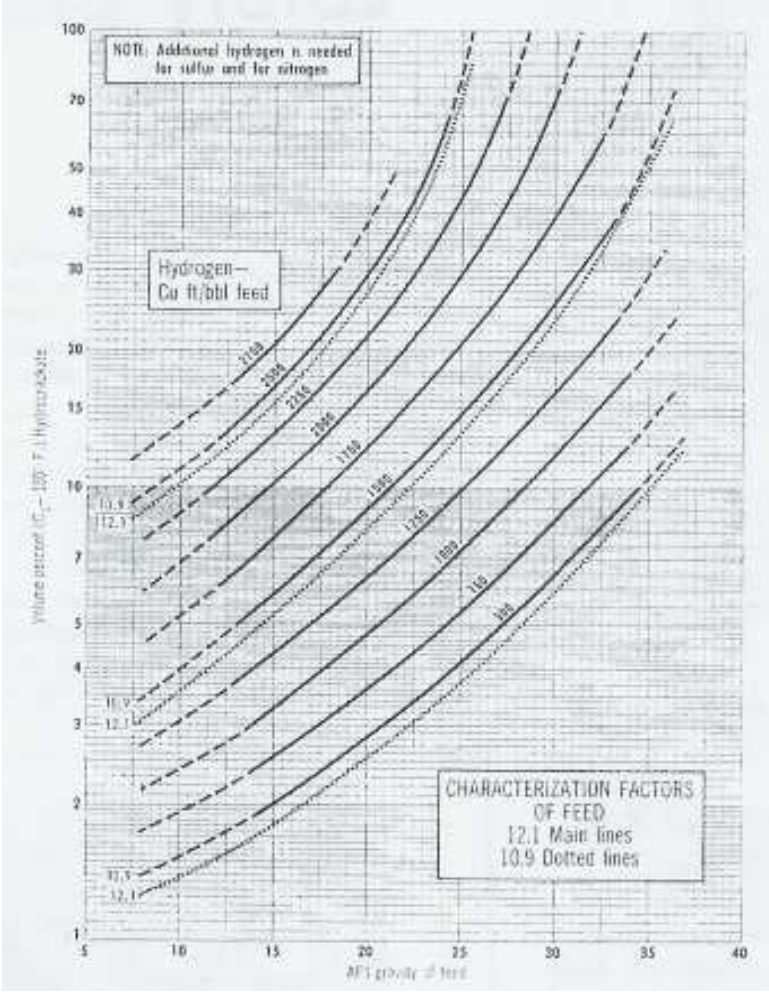
- Correlated data from “Oil and Gas Journal” W.L. Nelson
- Graphical correlated data was made continuous for hydrogen feed rate, Kw and API of the feed
- 3 inputs
- 5 outputs

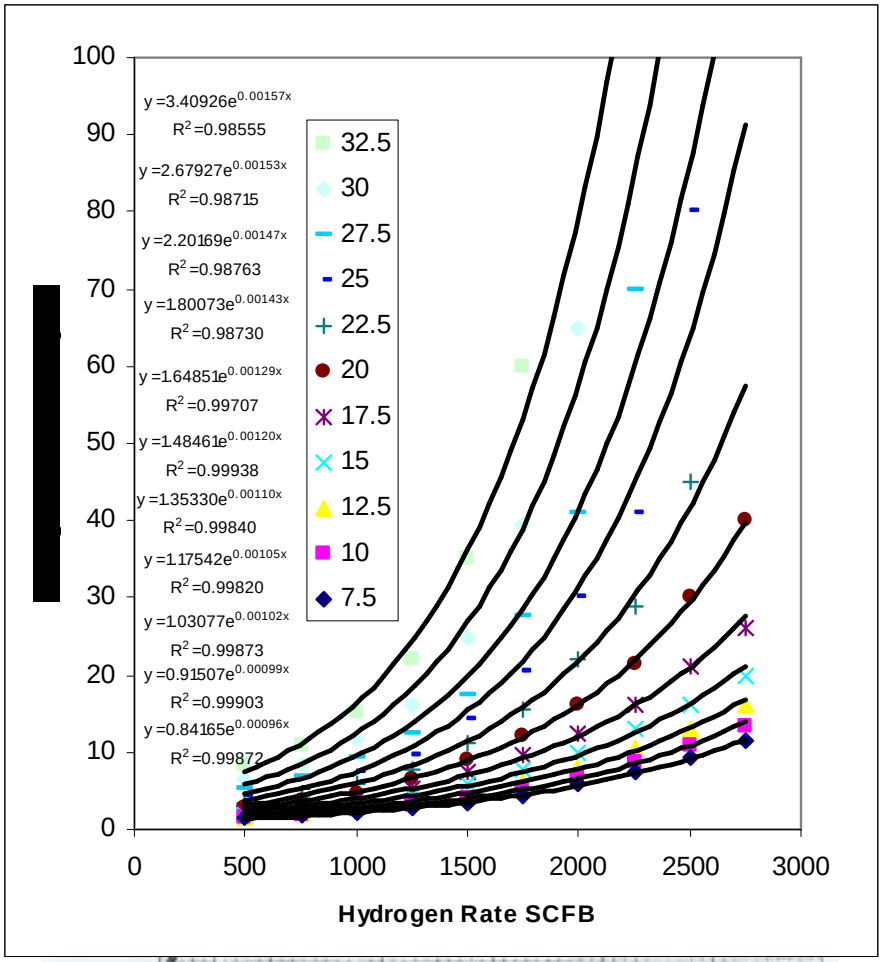
Hydrocracking Model

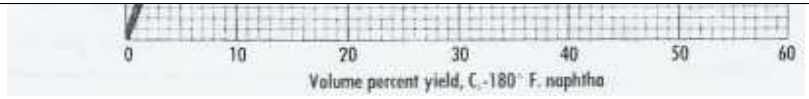




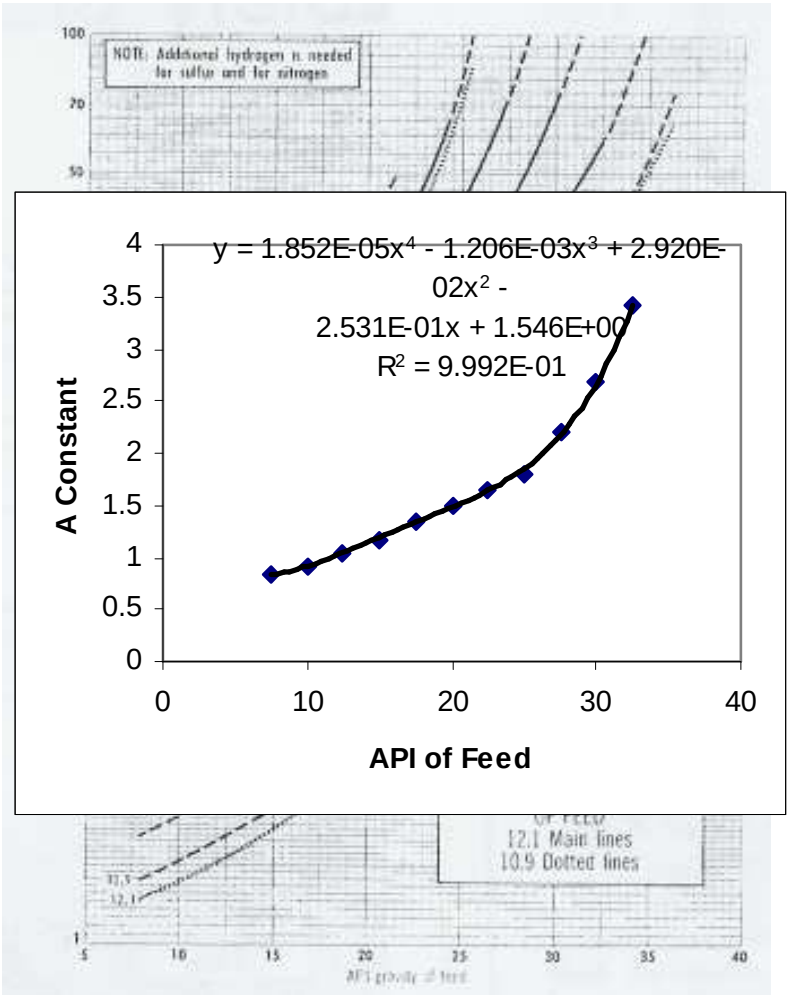
Hydrocracking Model

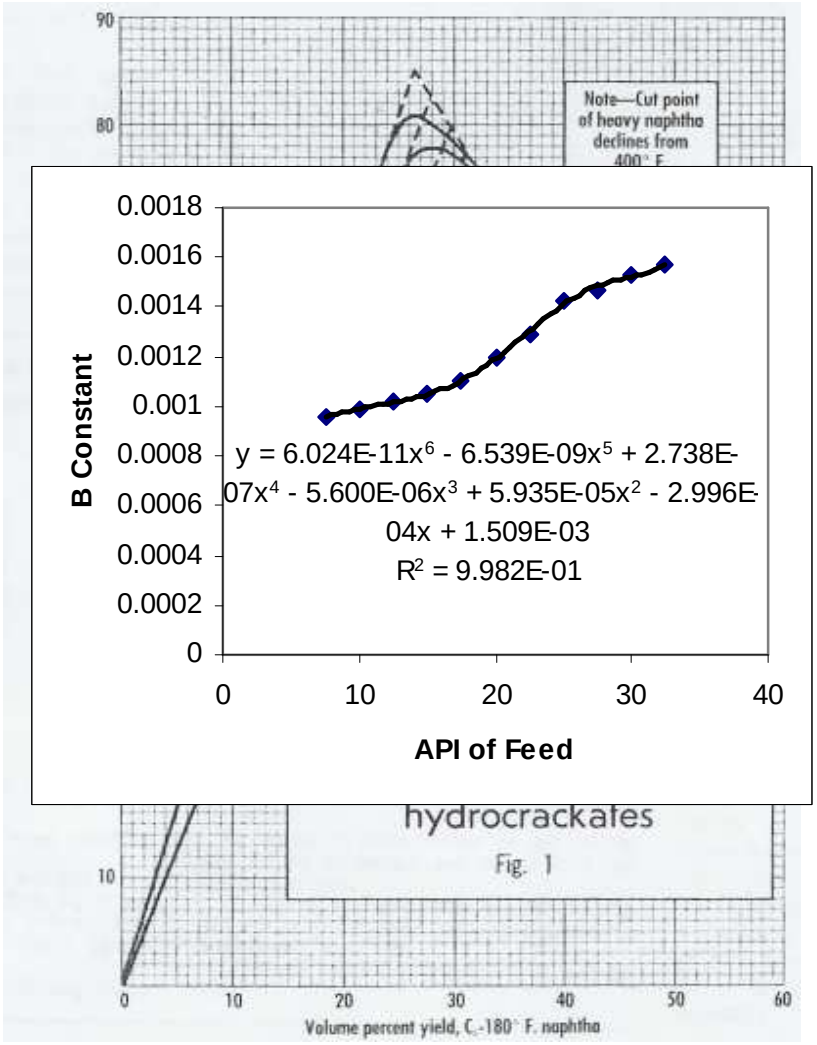




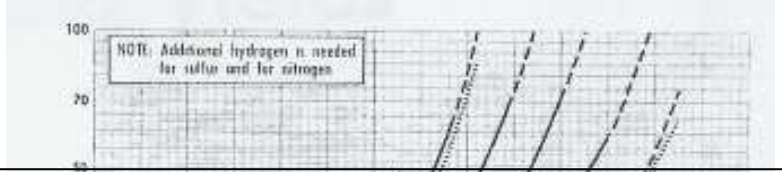


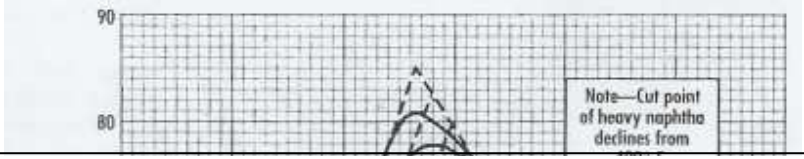
Hydrocracking Model





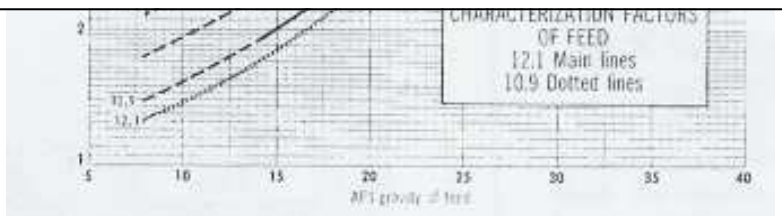
Hydrocracking Model

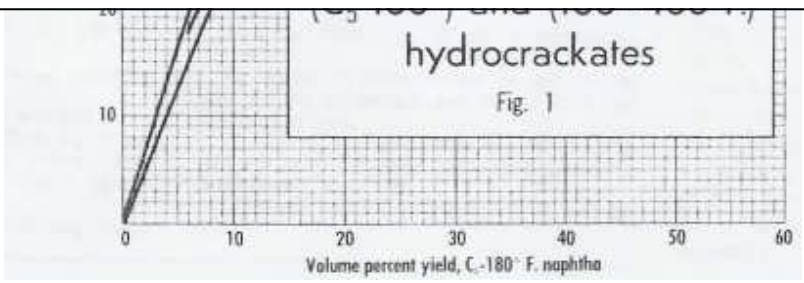




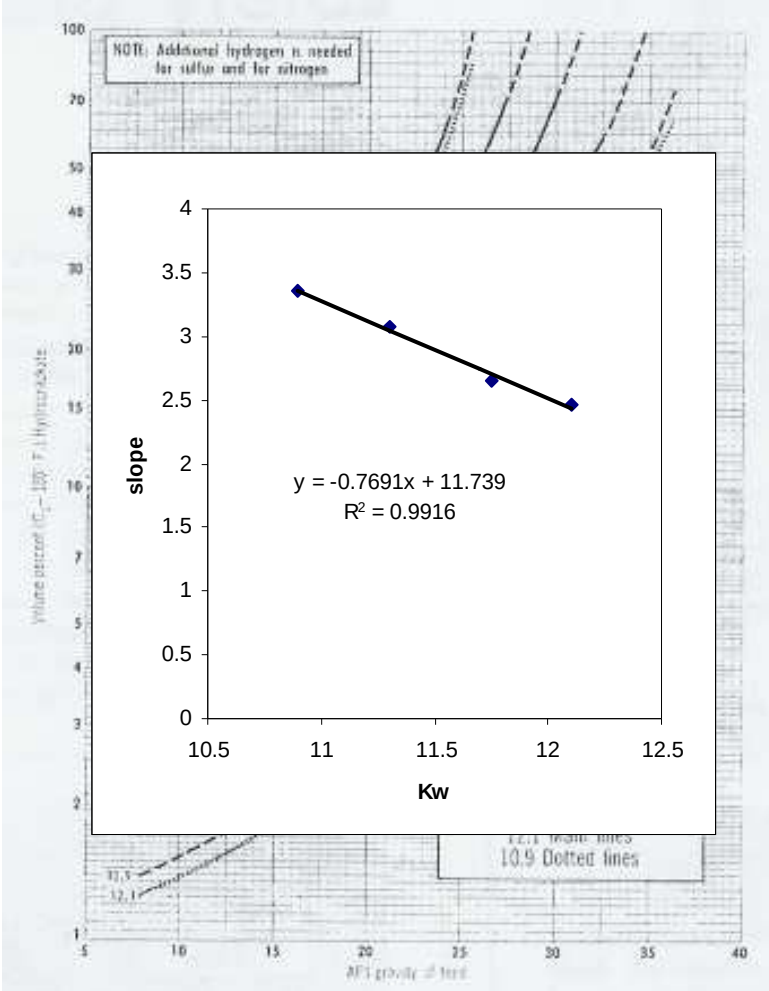
Vol% of light naptha

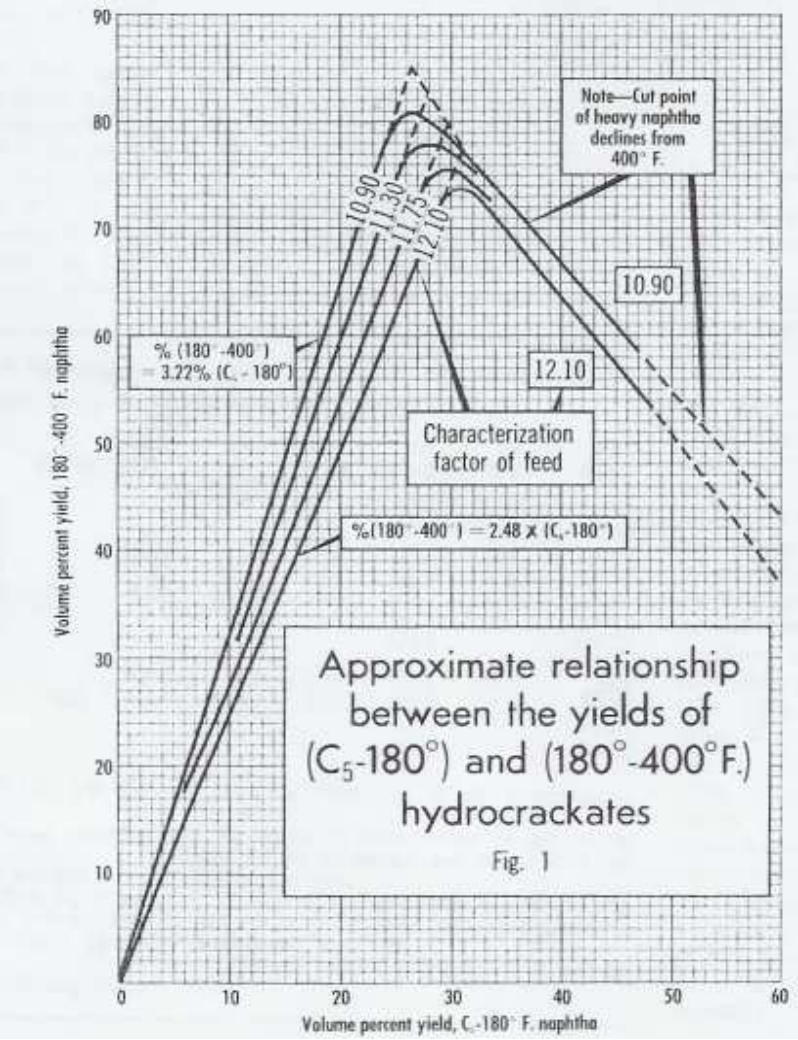
		°API							
Hydrogen Rate(SCFB)		7.5	10	12.5	15	17.5	20	22.5	25
2500	K_w=12.1	9.25	11	13	16	21	30	45	80
diff. from	K_w=10.9	0.75	1	1	1.25	1.75	2.5	5	7.5
		8.11%	9.09%	7.69%	7.81%	8.33%	8.33%	11.11%	9.38%
1500	K_w=12.1	3.4	4	4.8	5.8	7.3	9.1	11.25	14.25
diff. from	K_w=10.9	0.35	0.45	0.5	0.55	0.7	1	1.5	1.75
		10.29%	11.25%	10.42%	9.48%	9.59%	10.99%	13.33%	12.28%
500	K_w=12.1	1.4	1.55	1.7	2	2.3	2.8	3.4	4.2
diff. from	K_w=10.9	0.1	0.17	0.2	0.2	0.25	0.3	0.35	0.4
		7.14%	10.97%	11.76%	10.00%	10.87%	10.71%	10.29%	9.52%





Hydrocracking Model





Hydrocracking Equations

$$vol\%\,p_1 = (1.00833K_w - 0.00833)Ae^{B \bullet H}$$

$$vol\%\,p_2 = (-0.7691 \cdot \mathrm{K_w} + 11.739)(vol\%\,p_1)$$

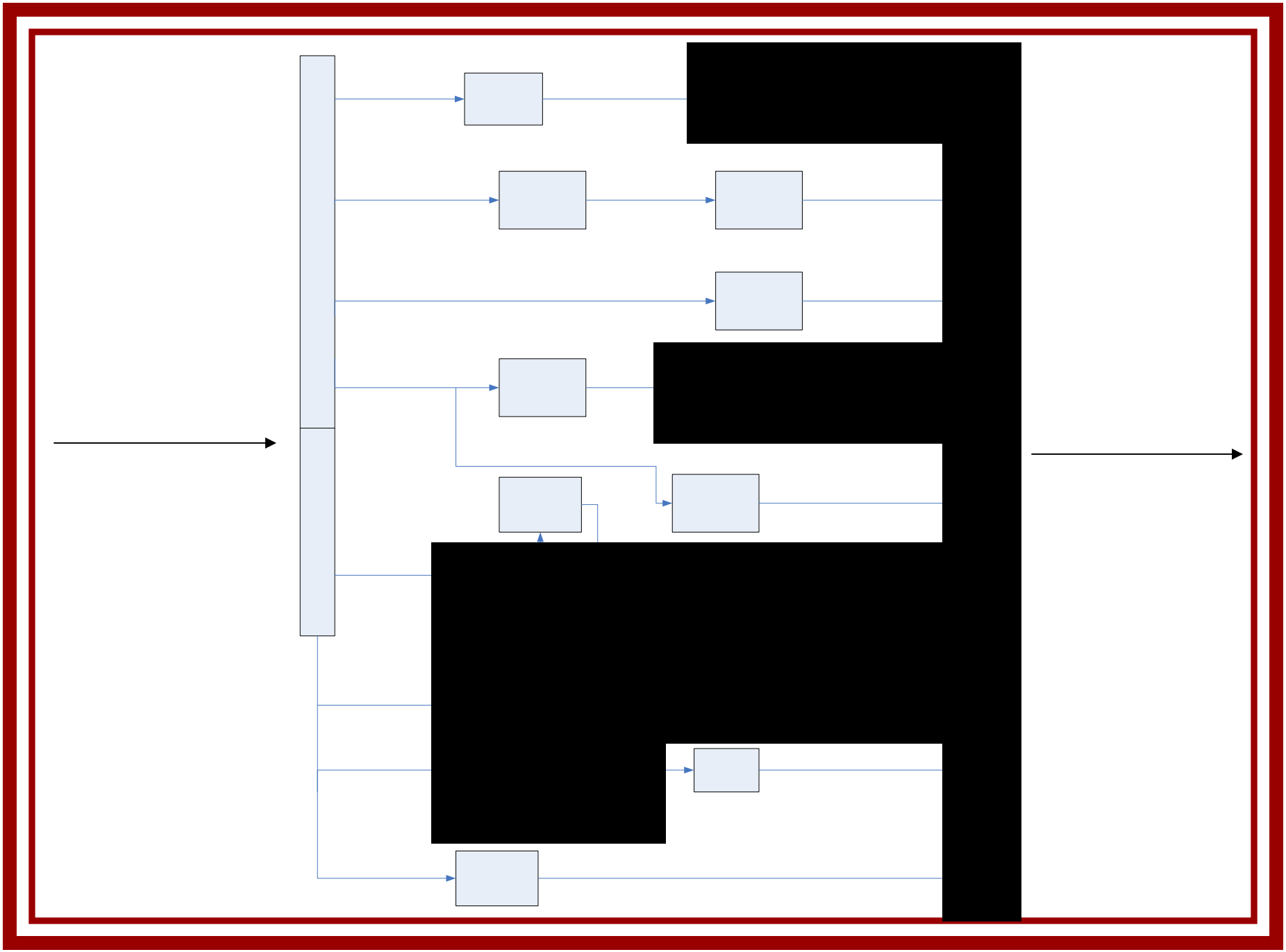
$$vol\%\,p_3 = 0.337(vol\%\,p_1)$$

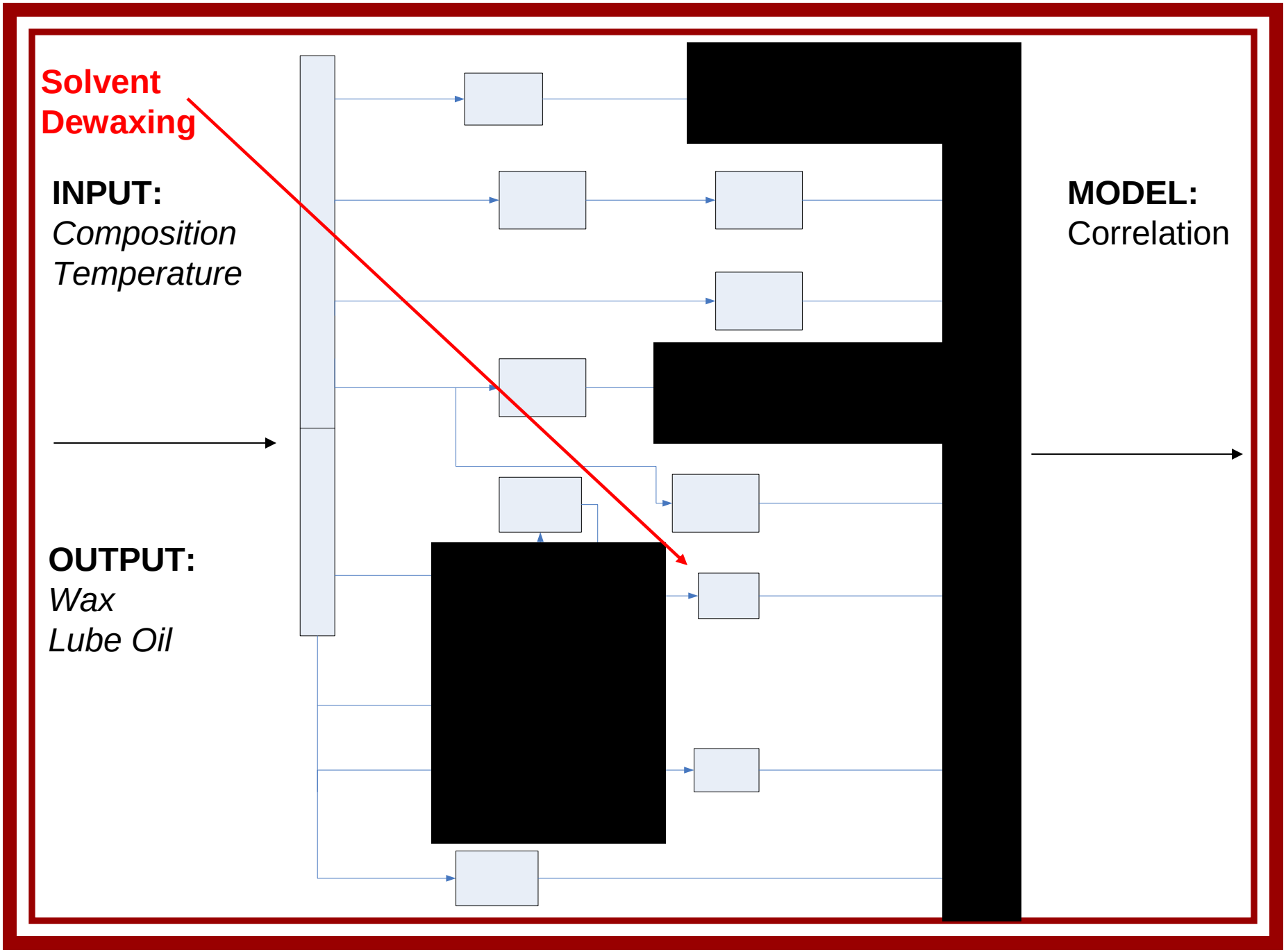
$$vol\%\,p_4 = 0.186(vol\%\,p_1)$$

$$vol\%\,p_5 = 1 + 0.09(vol\%\,p_1)$$

Hydrocracking Model

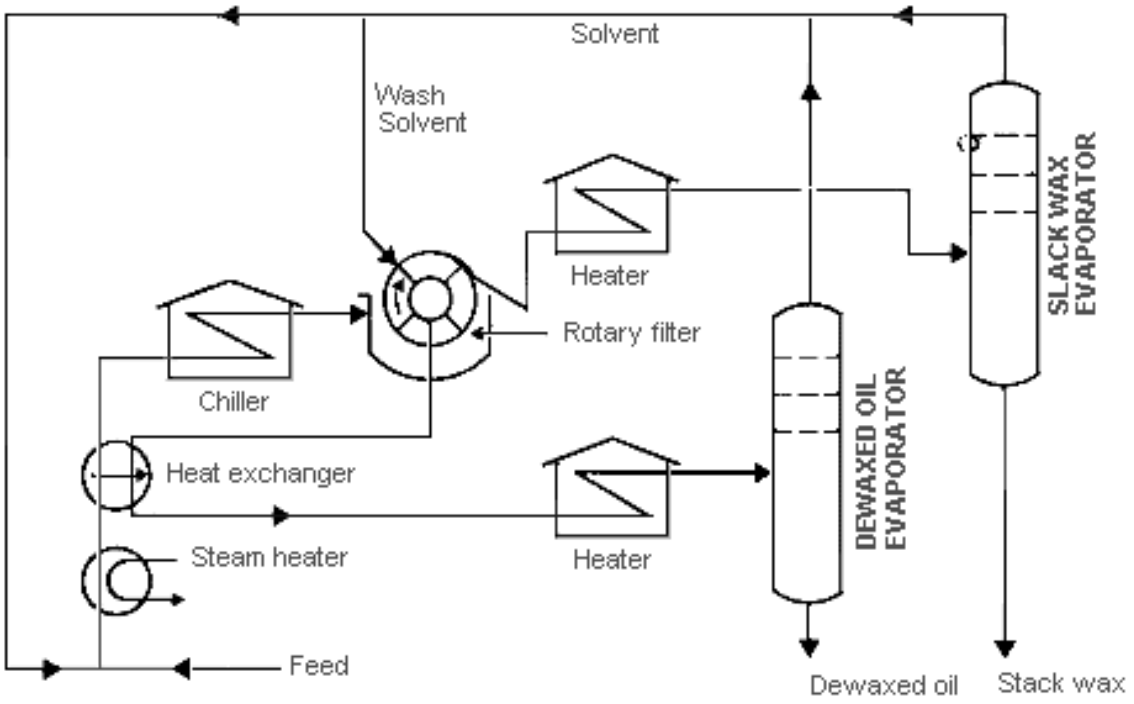
°API	Hydrogen (SCFB)	K_w	vol% p_1		vol% p_2	
15	2500	12.1	16.4	9%	39.9	1%
actual			15.0		40.5	
20	750	10.9	3.3	7%	11.0	9%
actual			3.5		10.0	
30	1250	10.9	16.3	25%	54.7	27%
actual			13.0		43.0	




Solvent Dewaxing
INPUT:
Composition
Temperature
OUTPUT:
Wax
Lube Oil
MODEL:
Correlation

Solvent Dewaxing

- Separate high pour point waxes from lubricating oils



Solvent Dewaxing

- Feedstocks
  - Distillate and residual stocks – heavy gas oils
  - Solvents – Ketones (MEK) and Propane
- Operating conditions
  - Solvent to oil ratio 1:1 to 4:1
  - Desired pour point of product

Dewaxing Model Development

- Correlation from “Energy and Fuels” Krishna et. al.
- 3 experimentally determined parameters
- 3 inputs
- 2 outputs

$$PPT = A0\log(100/PC) + A1/CL + A2$$

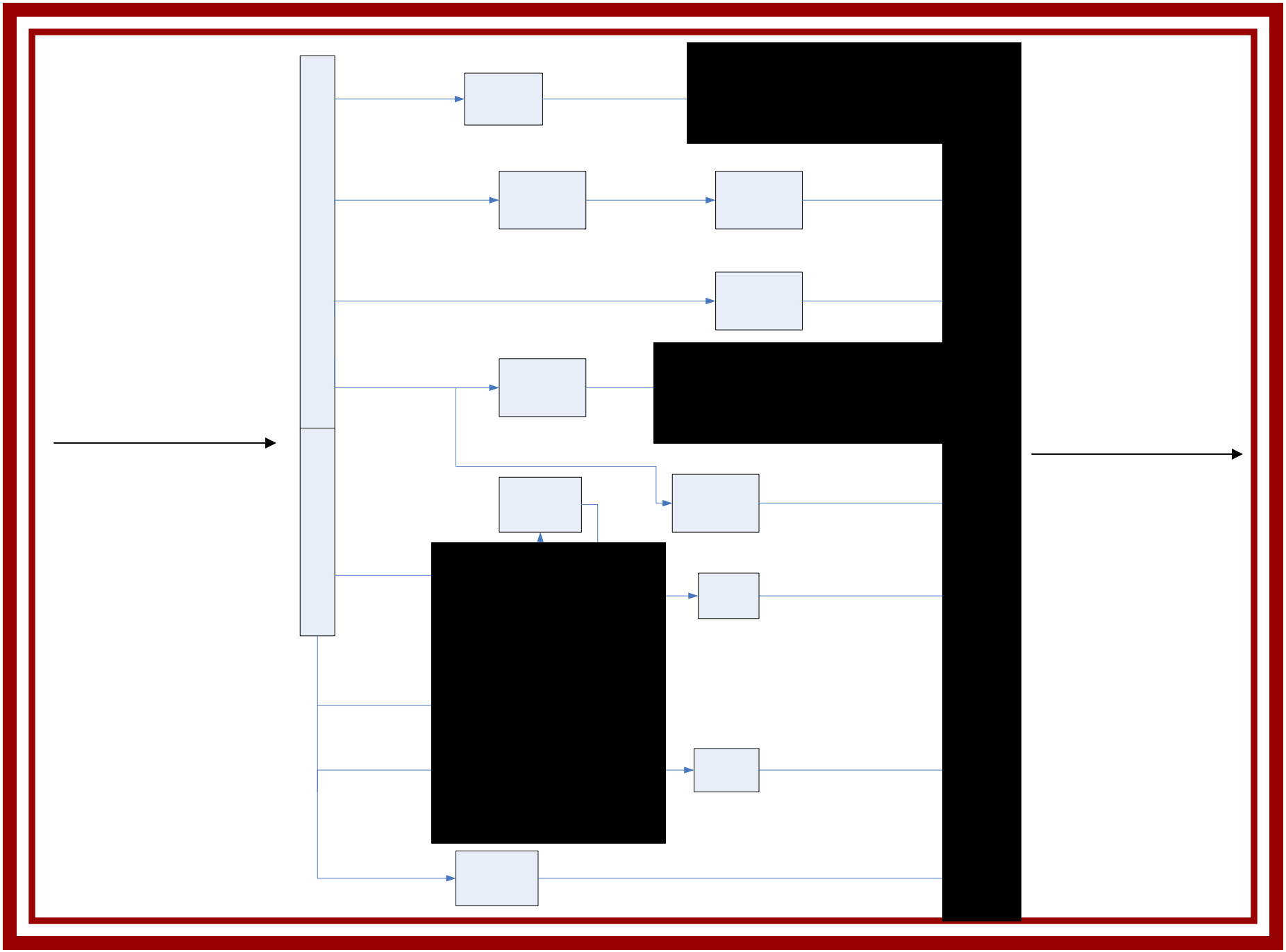
$$OilYield(wt\%) = \frac{(100 - PC(feed))}{(100 - PC(product))}$$

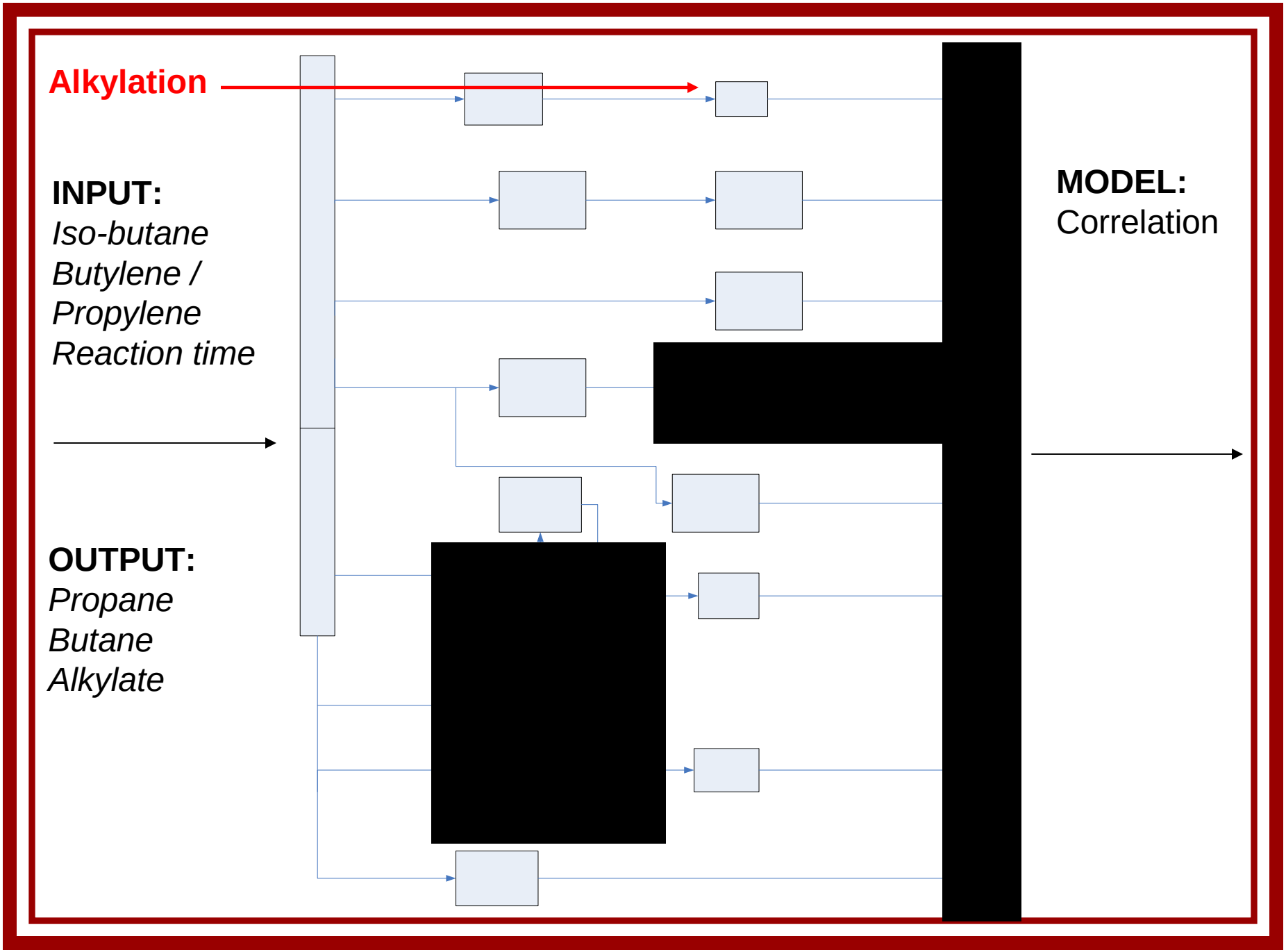
Dewaxing Model Error

	BC2	NC6	NC7	NC8	NC9	NC10
℃	375-500	375-400	400-425	425-450	450-475	475-500
wax wt%	46.8	44.88	47.28	48.41	48.72	47.05
CL	26.89	24.13	25.13	27.14	29.05	31
PPT act.	48	39	45	48	51	57
PPT pred.	48.0	41.0	44.0	48.9	52.8	55.9
error %	0.1%	5.0%	2.3%	1.8%	3.5%	1.9%

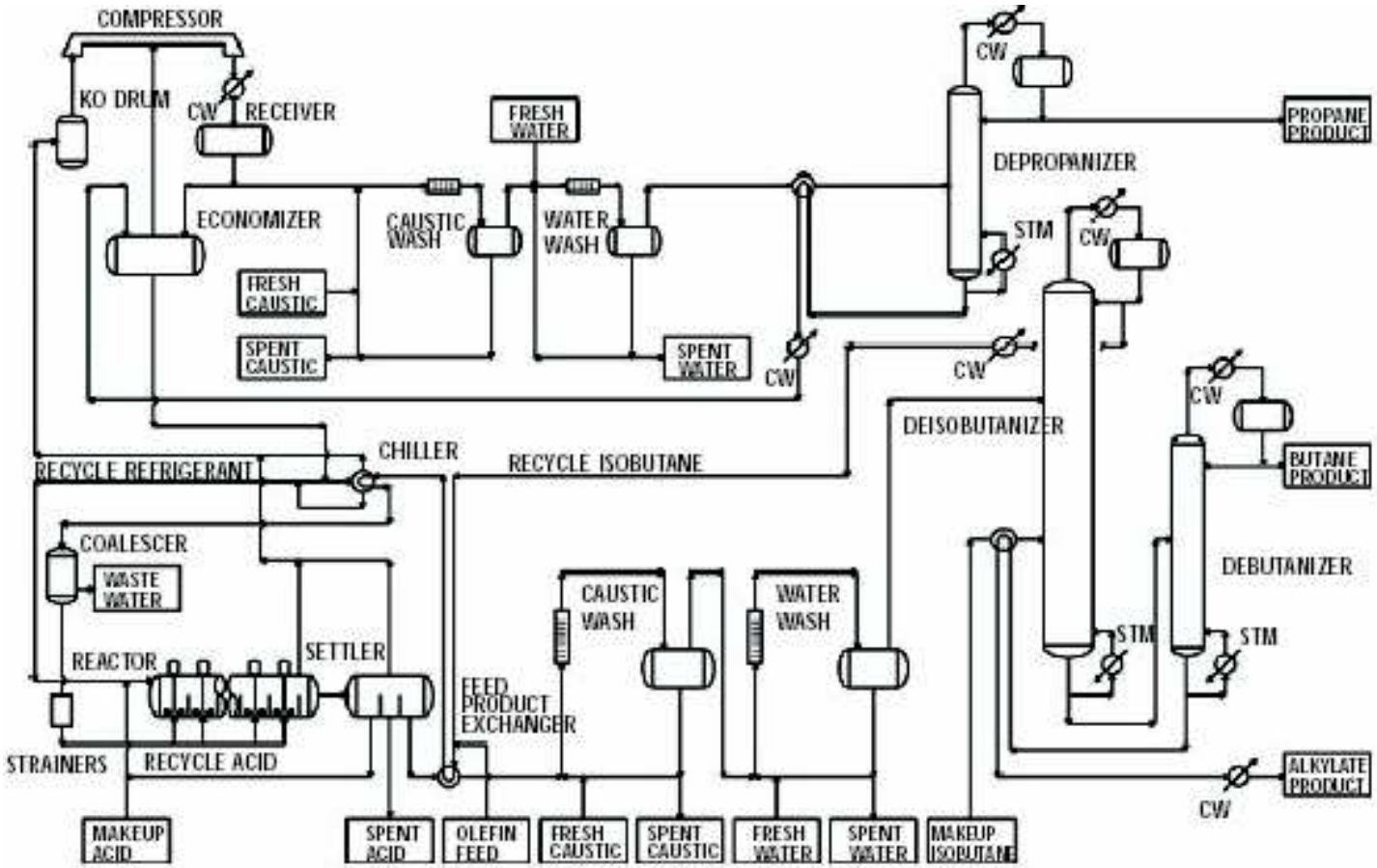
dewaxing model Desired PPT= 10

PPT low	9.99	9.50	9.77	9.82	9.65	9.81
PPT high	10.01	10.50	10.23	10.18	10.35	10.19
wax wt% low	0.368	0.819	0.608	0.336	0.202	0.133
wax wt% high	0.369	0.931	0.643	0.352	0.220	0.139
yield low	0.5340	0.5558	0.5304	0.5176	0.5138	0.5302
yield high	0.5340	0.5564	0.5306	0.5177	0.5139	0.5302
error %	0.001%	0.112%	0.036%	0.016%	0.019%	0.006%




Alkylation
INPUT:
Iso-butane
Butylene /
Propylene
Reaction time
OUTPUT:
Propane
Butane
Alkylate
MODEL:
Correlation

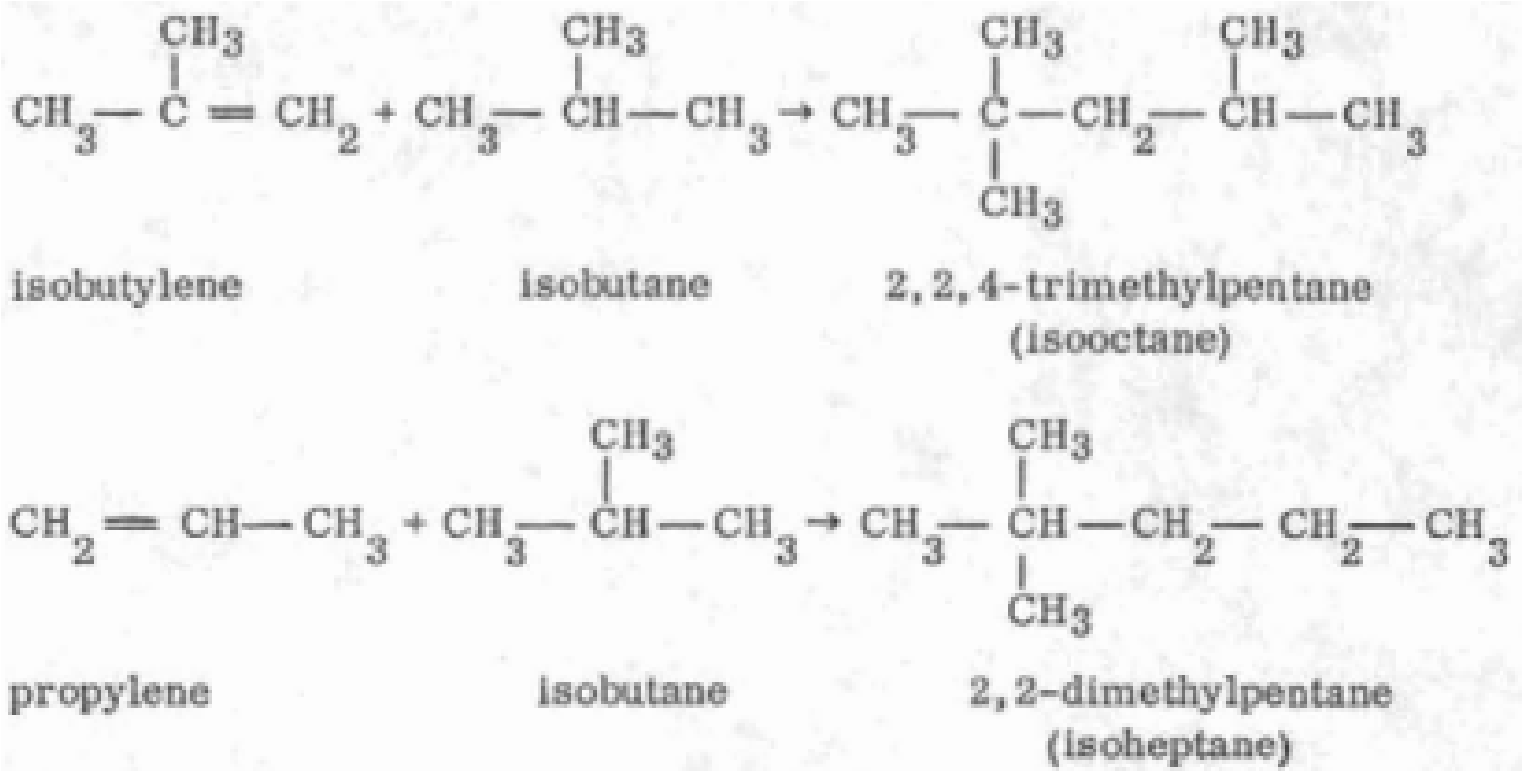
Alkylation PFD



Exxon-Mobil Autorefrigeration H_2SO_4 alkylation

http://www.prod.exxonmobil.com/refiningtechnologies/pdf/AlkyforWR02.pdf

Alkylation



*Lots of side reactions

Alkylation

$$F = \frac{I_E (I/O)_F}{100(SV)_O}$$

$(I/O)_F$ = volumetric isobutane/olefin ratio in feed

I_E = isobutane in reactor effluent, liquid volume %

$(SV)_O$ = olefin space velocity, v/hr/v

F= Factor defined by A.V. Mrstik

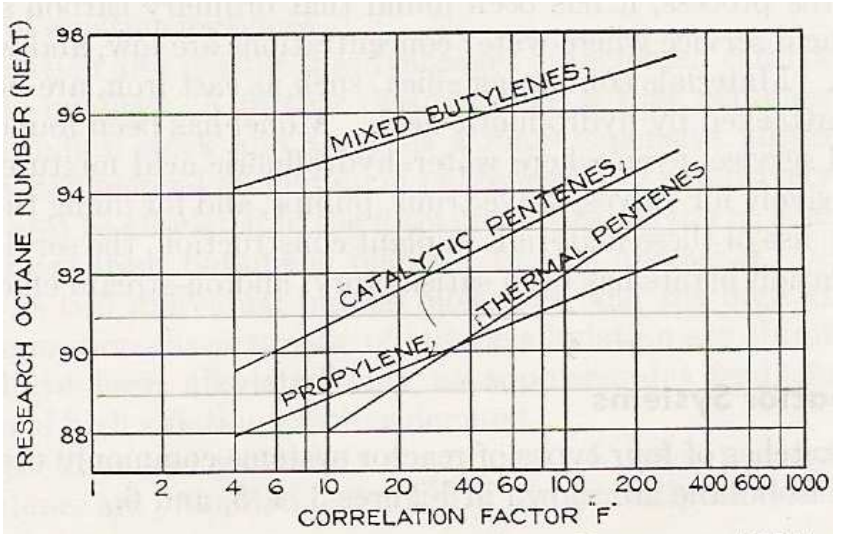
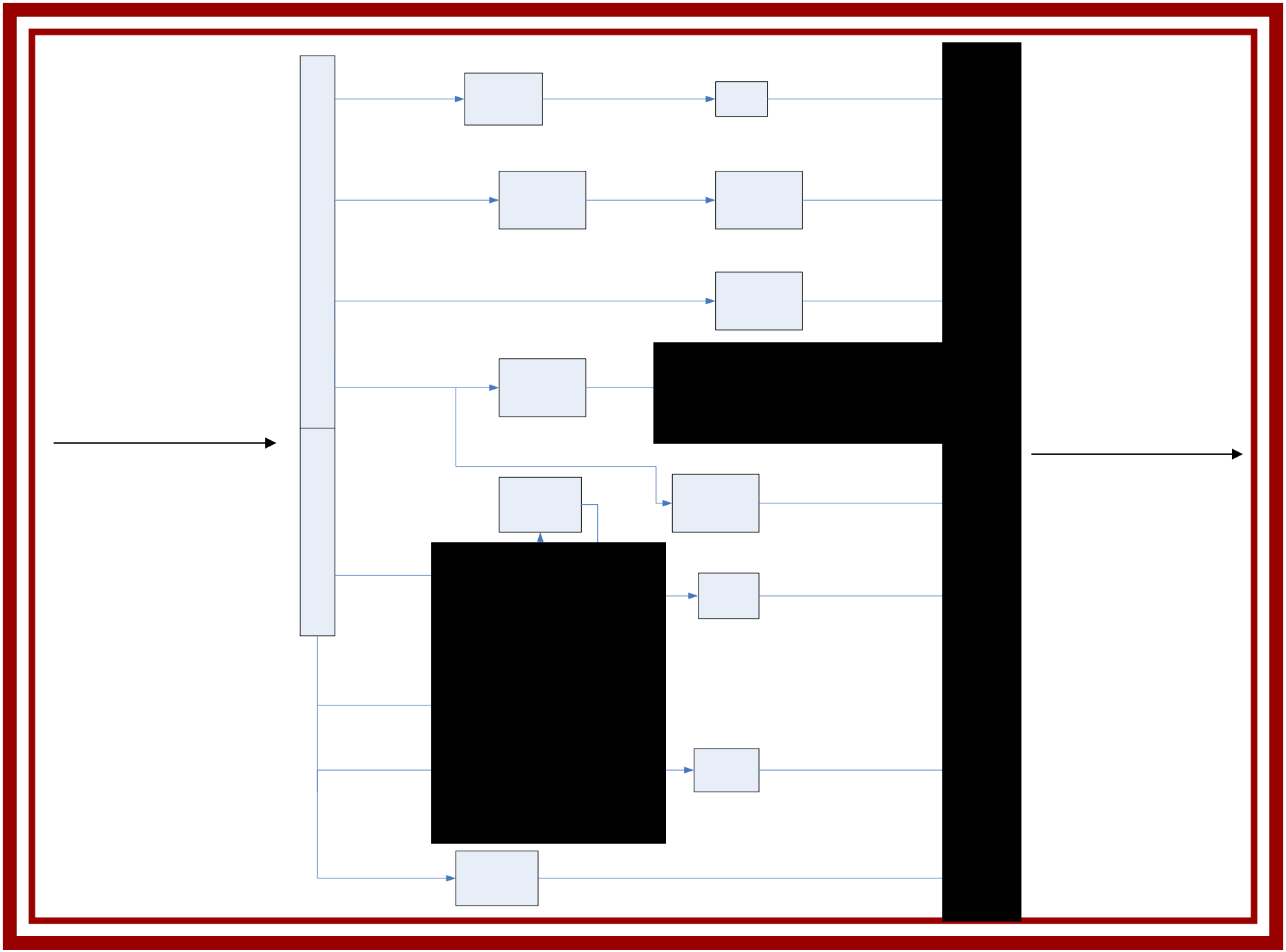
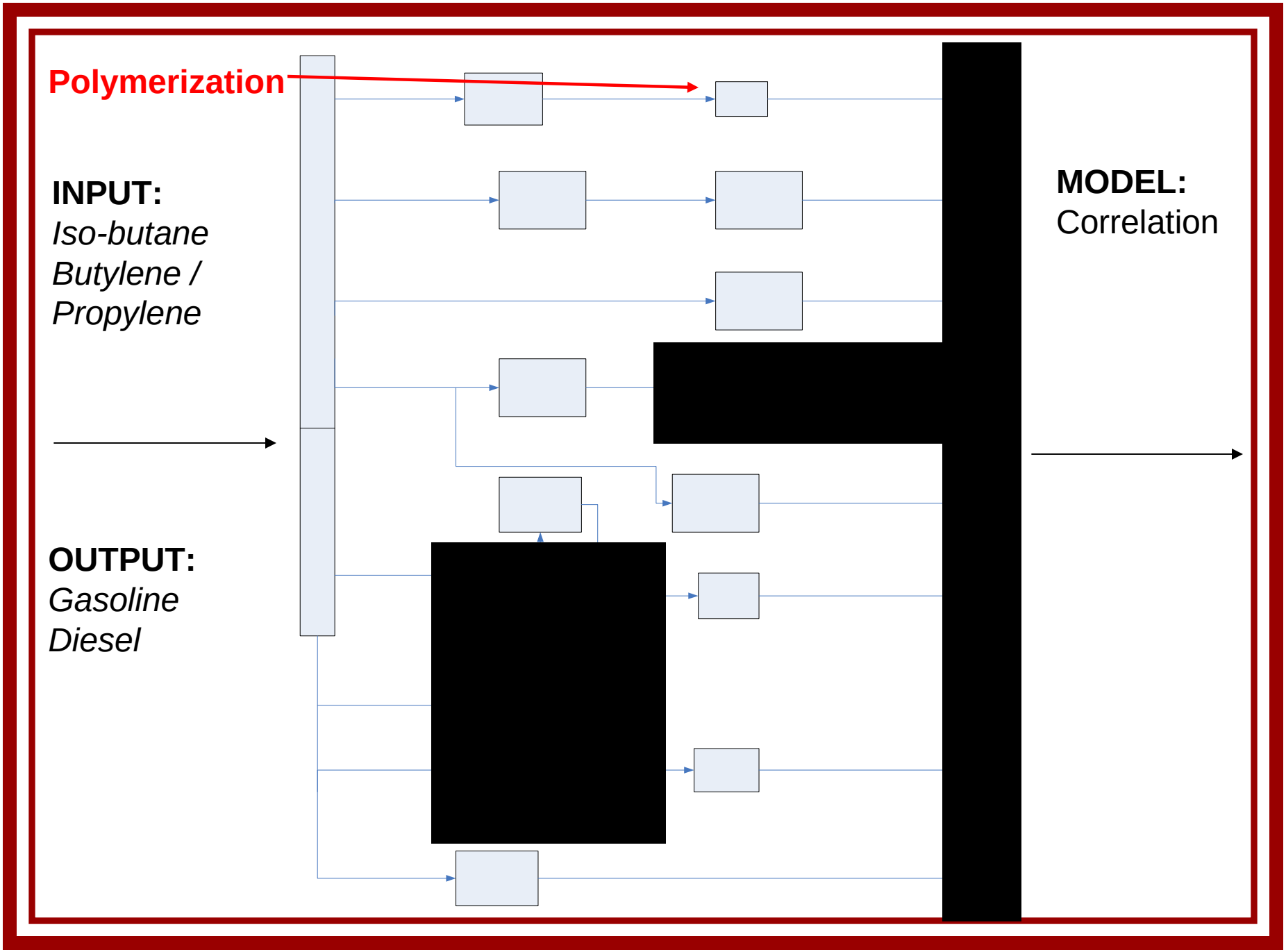


Figure 7. Sulfuric Acid Alkylate Octanes, ASTM Research (CRC-F-1)

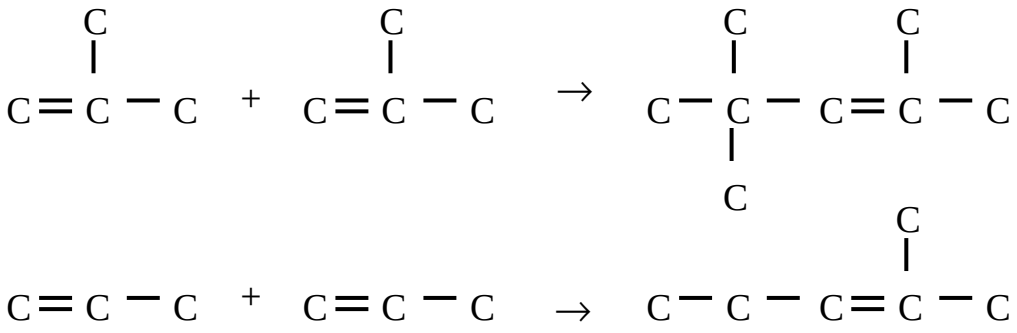
"Progress in Petroleum Technology" AV Mrstik et al. ACS Publications




Polymerization
INPUT:
Iso-butane
Butylene /
Propylene
OUTPUT:
Gasoline
Diesel
MODEL:
Correlation

Polymerization

- Converts Propylenes and butylenes into saturated carbon chains
- 1st used Catalytic Solid Phosphoric Acid (SPA) on silica fell out of popularity in 1960s.
- Now experimenting with Zeolites.



- Polymerization reaction is highly exothermic and temperature is controlled either by injecting cold propane quench or by generating steam.
- Propane is also recycled to help control temperature

CO School of Mines http://jechura.com/ChEN409/11%20Alkylation.pdf
http://www.personal.psu.edu/users/w/y/wyg100/fsc432/Lecture%2015.htm

Zeolite Polymerization

- Converts propylenes and butylenes into saturated carbon chains by means of zeolite catalysis (ZSM-5)

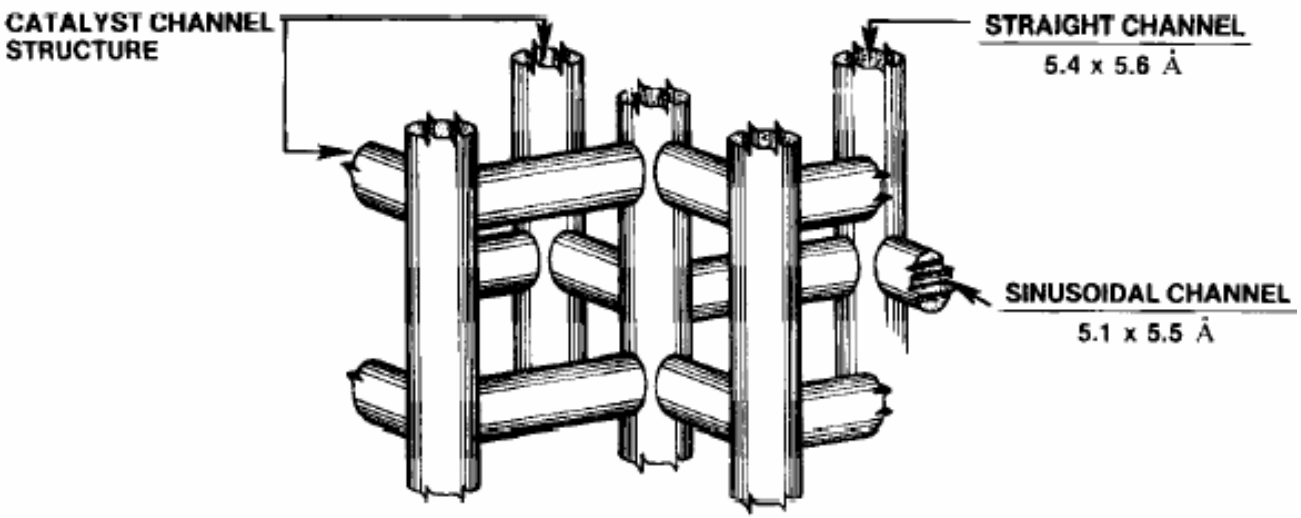
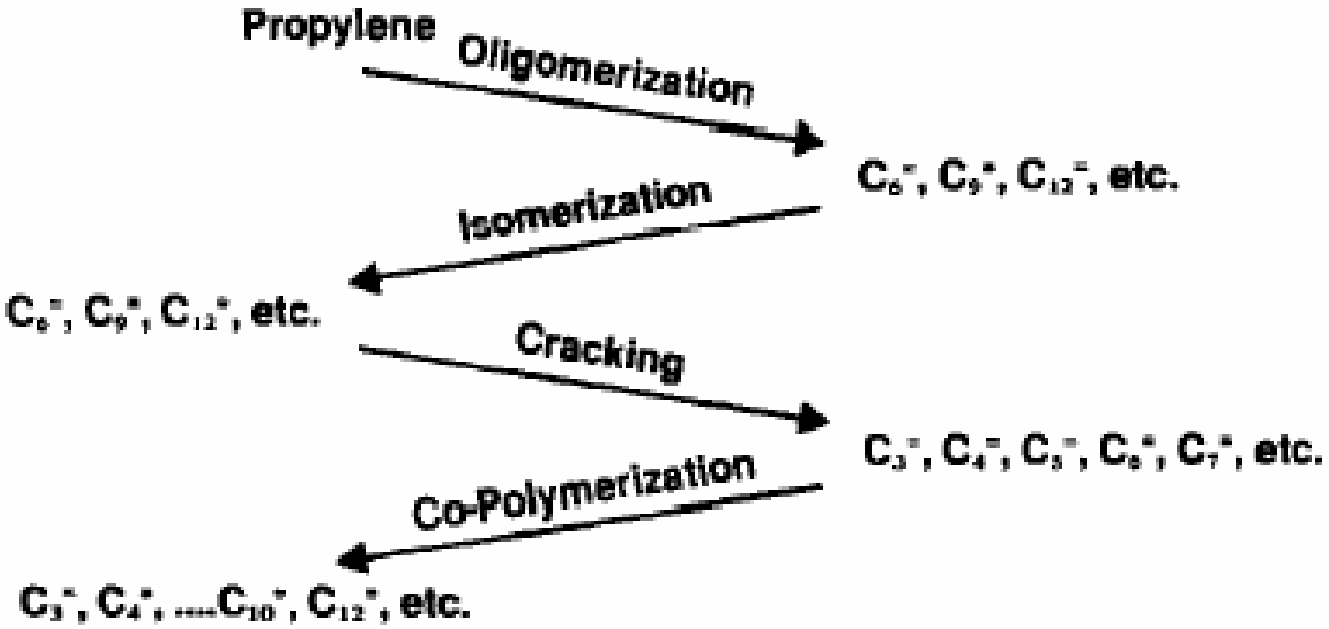


Figure 1. ZSM-5 Catalyst.

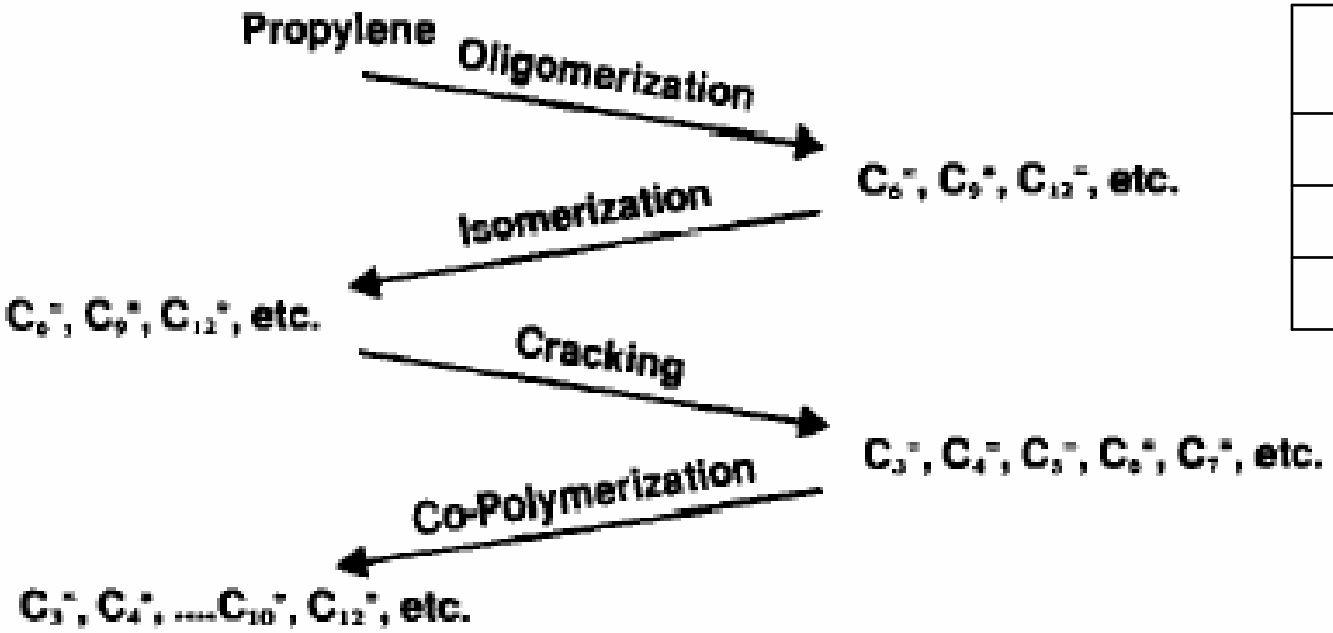
Zeolite Polymerization

- Converts propylenes and butylenes into saturated carbon chains by means of zeolite catalysis (ZSM-5)



Zeolite Polymerization

- Converts propylenes and butylenes into saturated carbon chains by means of zeolite catalysis (ZSM-5)



Specific Gravity	0.73
Octane	
RON	92
MON	79

[Tabak, 1986]

Zeolite Polymerization

Charge

- 17wt.% Propylene
- 10.7 wt.% Propane
- 36.1 wt.% 1-butene
- 27.2 wt.% isobutane

Temperature = 550K

Total Pressure = 5430 kPa

Propylene partial pressure = 7~3470kPa.

*Depending on desired chain length

Zeolite Polymerization

Charge

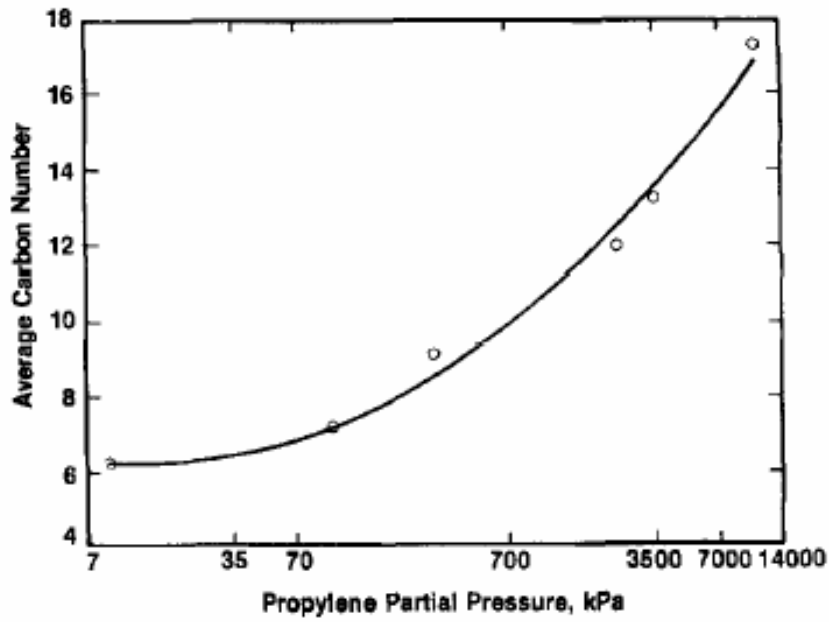
- 17wt.% Propylene
- 10.7 wt.% Propane
- 36.1 wt.% 1-butene
- 27.2 wt.% isobutane

Temperature = 550K

Total Pressure = 5430 kPa

Propylene partial pressure = 7~3470kPa.

*Depending on desired chain length



Polymerization

+ PBR-gas phase

- *Solid catalysis*

+ Produce either diesel or gasoline range chains

- *Typical octane number = 92 (RON)*

vs

Alkylation

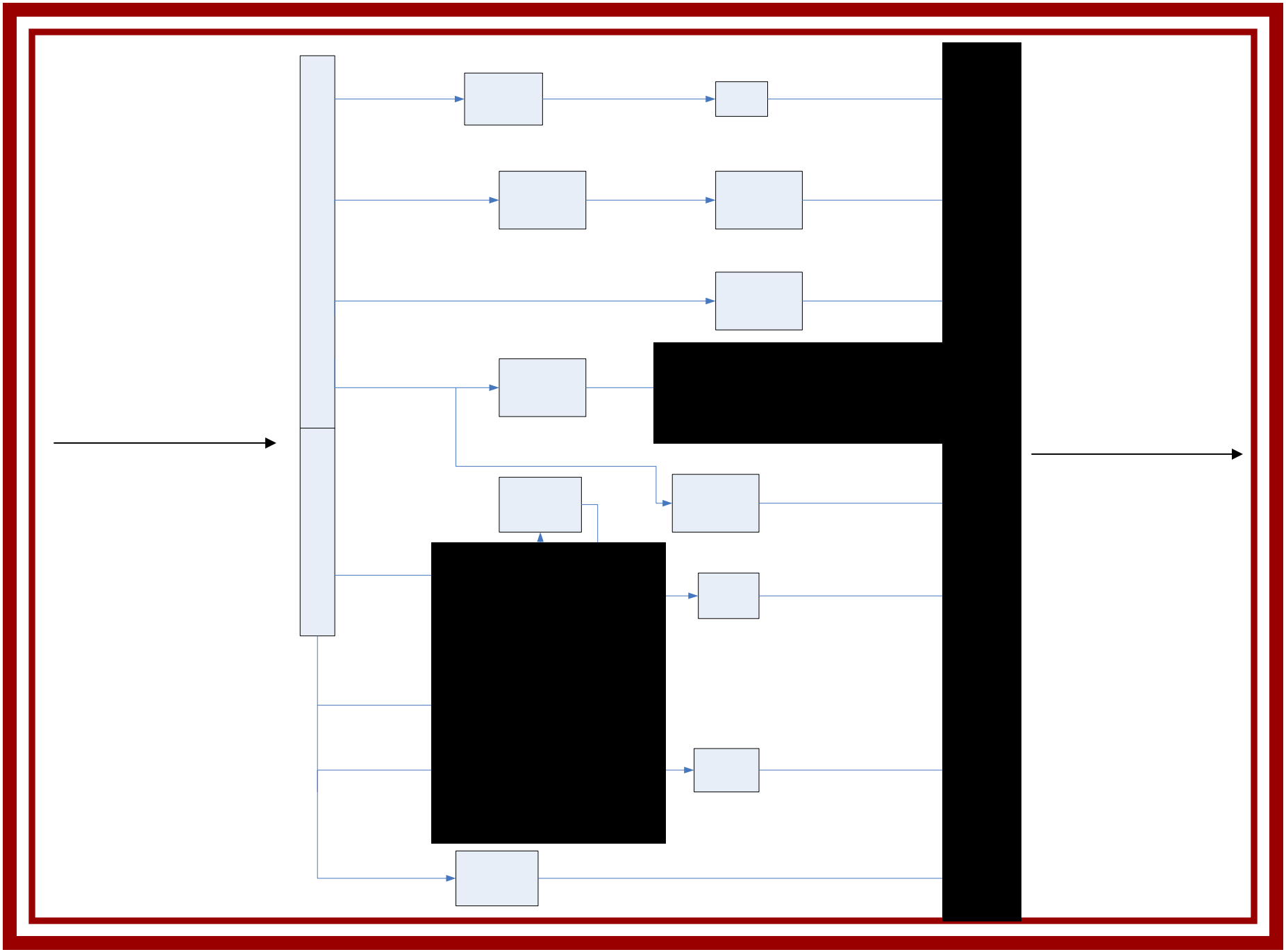
- *CSTR- liquid phase*

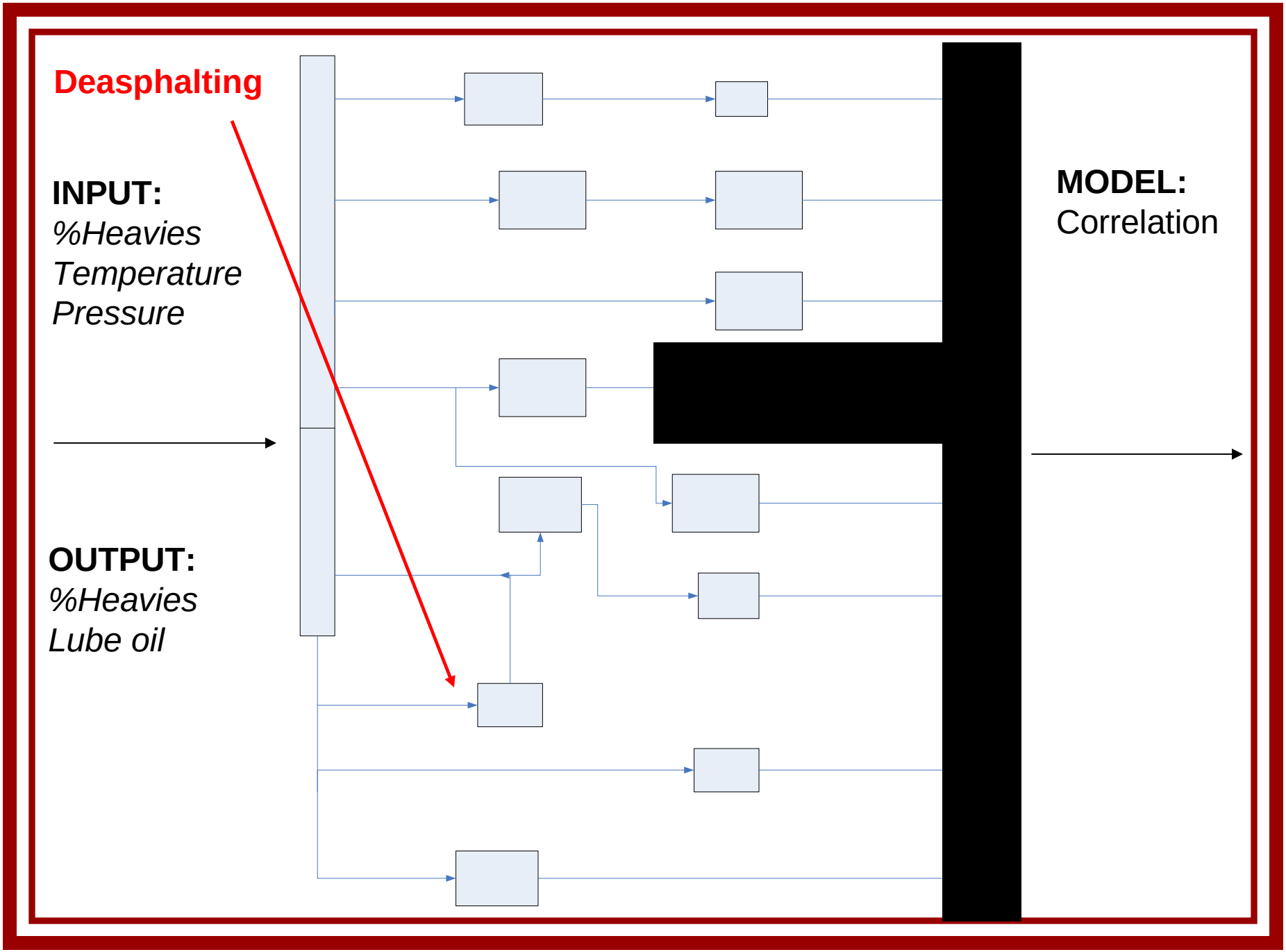
+ Liquid catalysis

- *Requires very vigorous agitation*

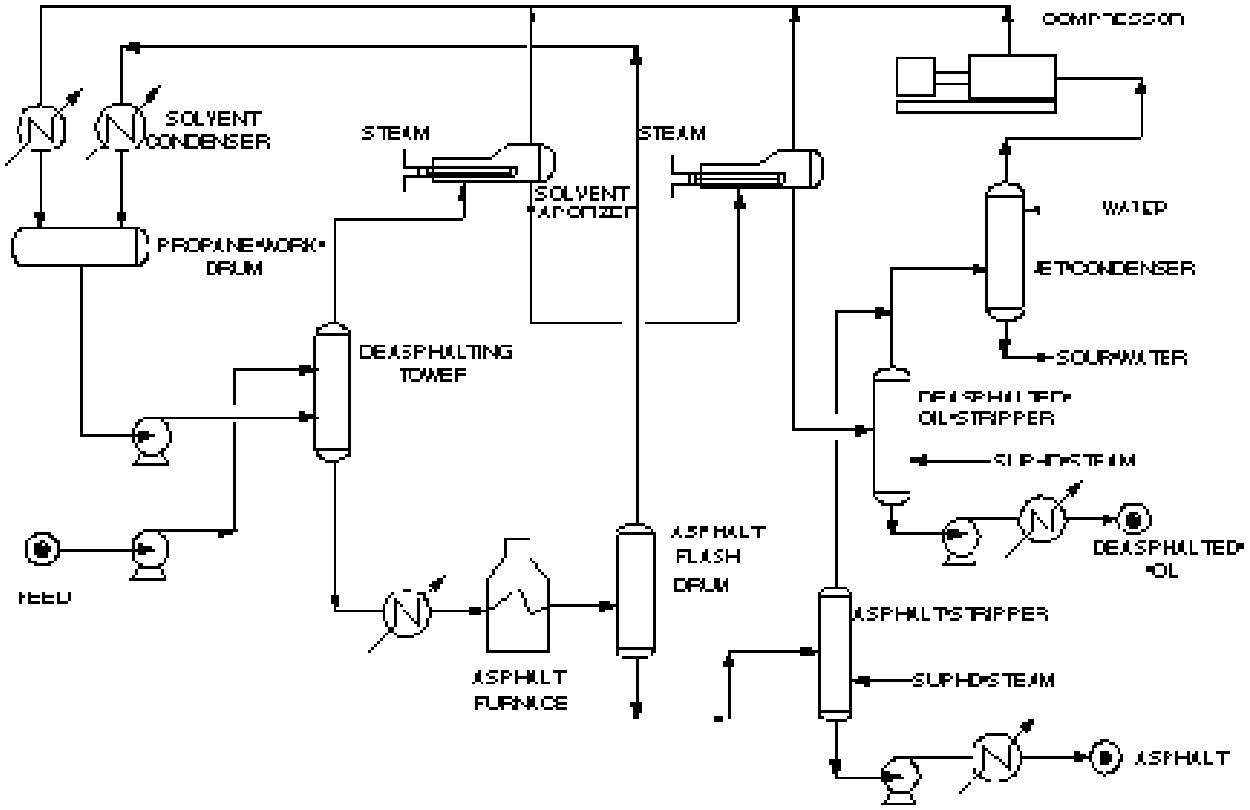
- *Typically .1lb$_m$ acid consumed per gallon product*

++Typical octane number = 96(RON)




Deasphalting
INPUT:
%Heavies
Temperature
Pressure
OUTPUT:
%Heavies
Lube oil
MODEL:
Correlation

Propane Deasphalting - PFD



Typical Propane Deasphalting

http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322000000300012&lng=pt&nrm=iso

Propane Deasphalting

Types

1. Sub Critical. (below 369K) Modeled first by Robert E. Wilson in 1936. Hildebrand solubility parameters now used.
2. Super Critical. (above 369K) Now popular. High selectivity. No good model.

Both remove greater than 99% asphalt

Sub Critical Propane Deasphalting

Hildebrand solubility

$$\delta = \left(\frac{\Delta H - R_g T}{V} \right)^{1/2}$$

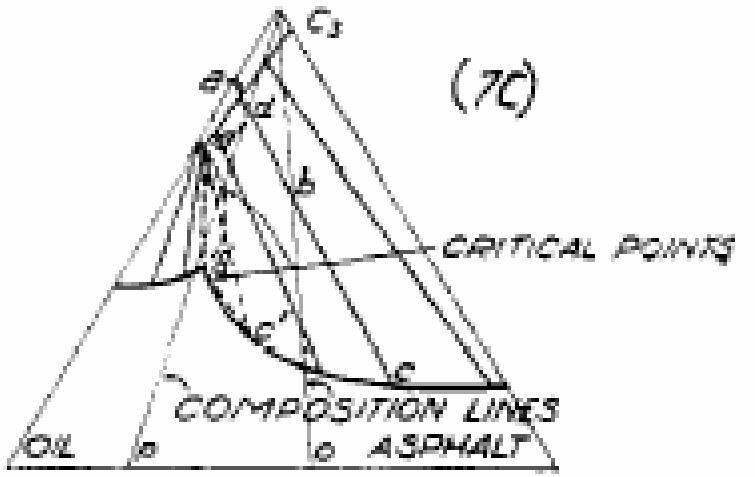
δ = Solubility Parameter [J/mol]

ΔH = Heat of vaporization [J/mol]

R_g = Universal gas Constant [8.314J/mol/K]

T = Temperature [K]

V = molar volume [L/mol]



ISOTHERM AT 180°F

FIG. 7. IDEALIZED DIAGRAM FOR THE SYSTEM PROPANE-OIL-ASPHALT

Super Critical Propane Deasphalting

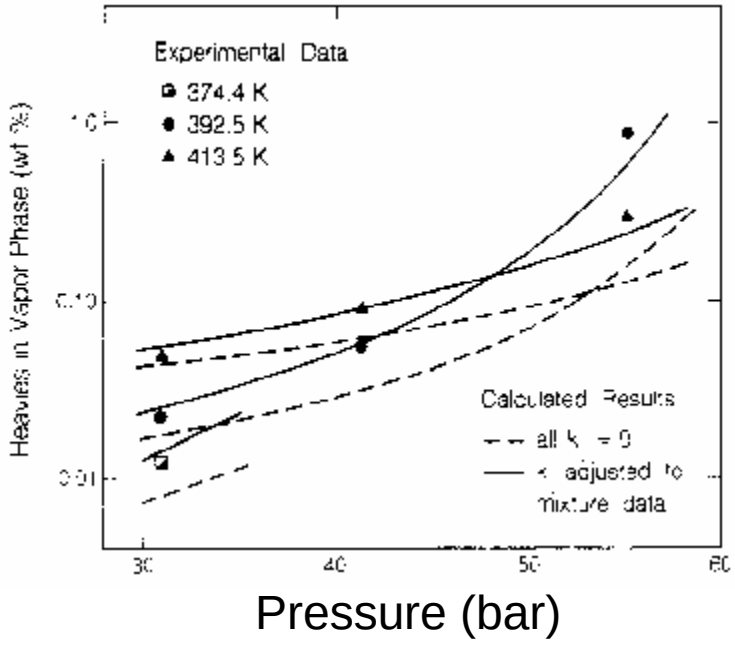
Models typically break down near the critical point. Including Redlick-Kwong, Soave-Redlick-Kwong and Perturbed-Hard-Chain (PHC). Therefore correlations have to be used.

<u>Typically operate at</u>

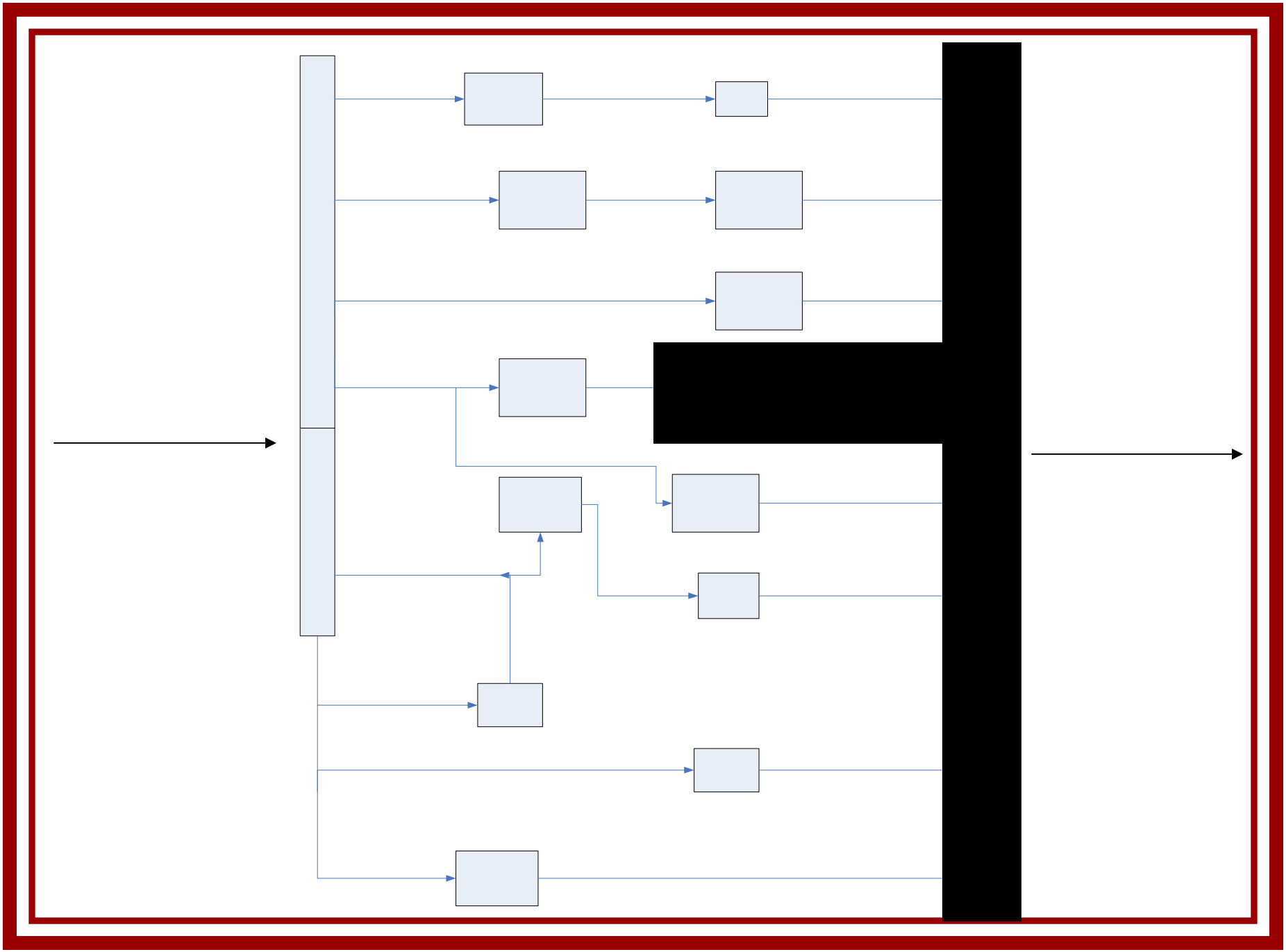
T=400K

Pressure=55 bar

Ratio= 4:1 propane to oil mixture



"Phase Equilibria in Supercritical Propane Systems for Separation of Continuous Oil Mixtures" Radosz, Maciej et al. Ind. Eng. Chem. Res. 1987, 26, 731-737

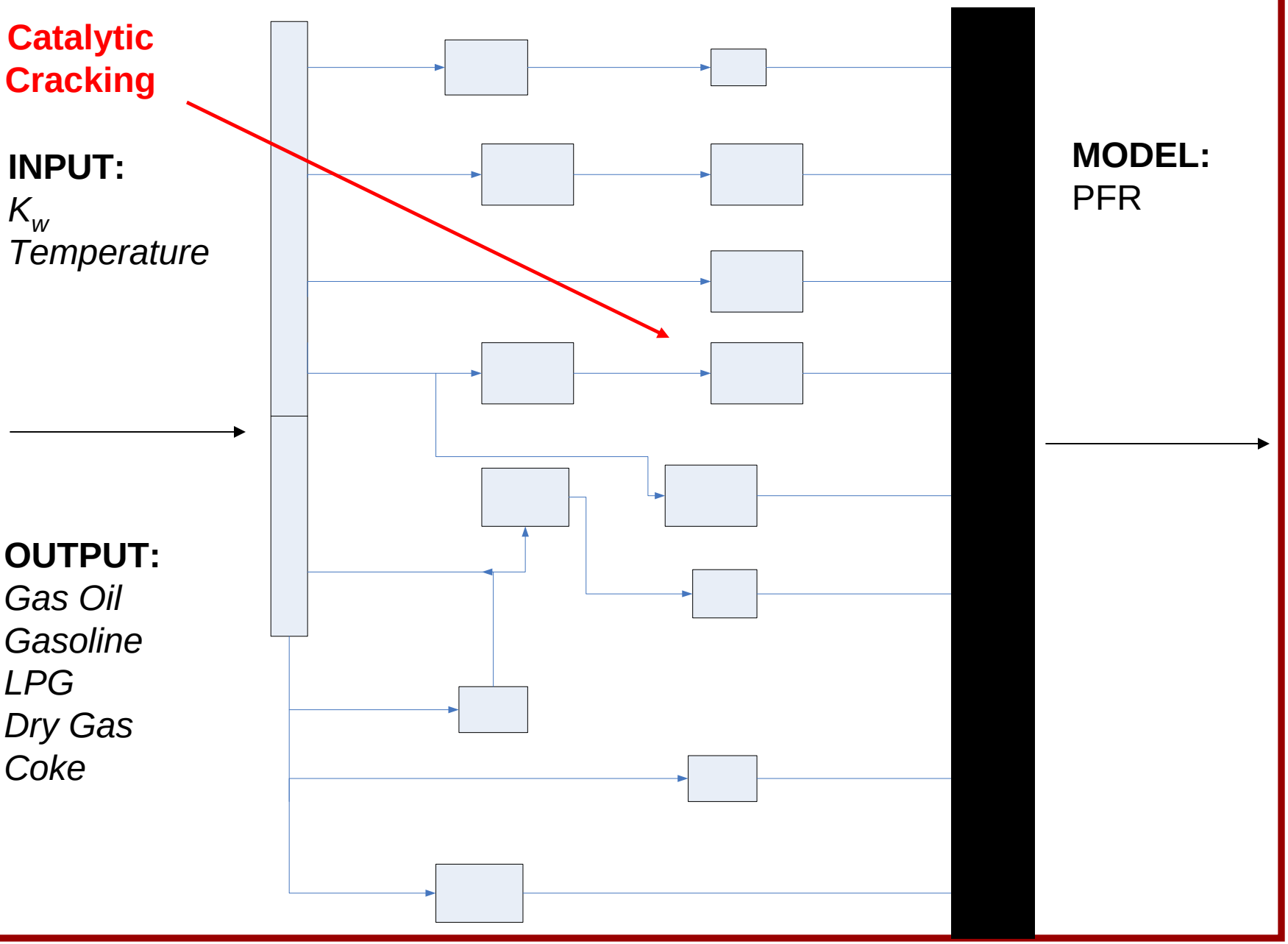


Catalytic Cracking

INPUT:

K_w

Temperature



MODEL:

PFR

OUTPUT:

Gas Oil

Gasoline

LPG

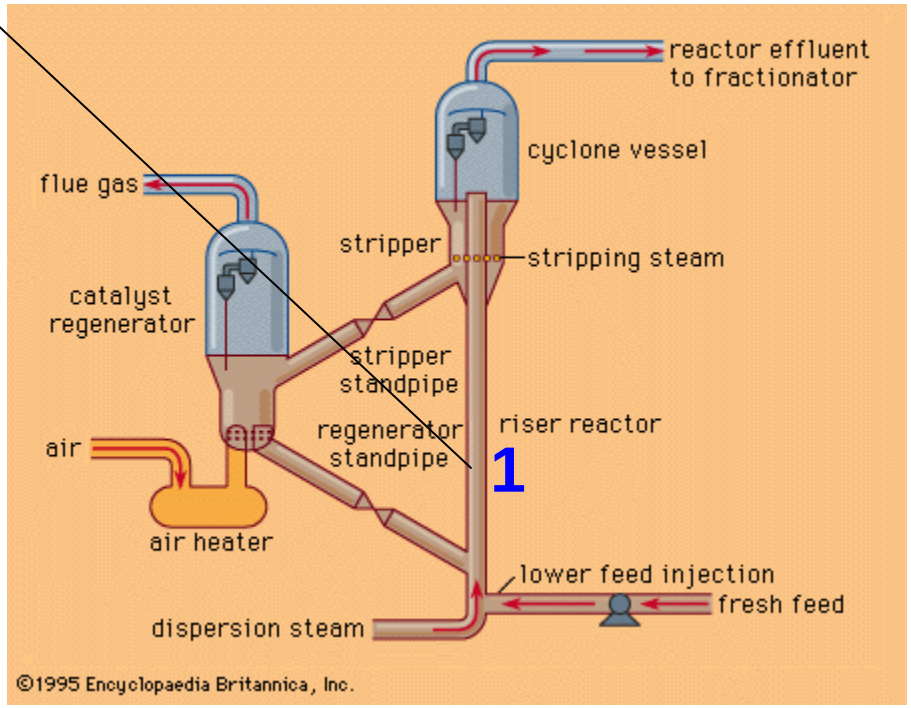
Dry Gas

Coke

Fluidized Catalytic Cracking

- Pretreated feedstock is fed into the bottom of the riser tube where it meets very hot regenerated catalyst.

- The feed vaporizes and is cracked as it passes up the riser.



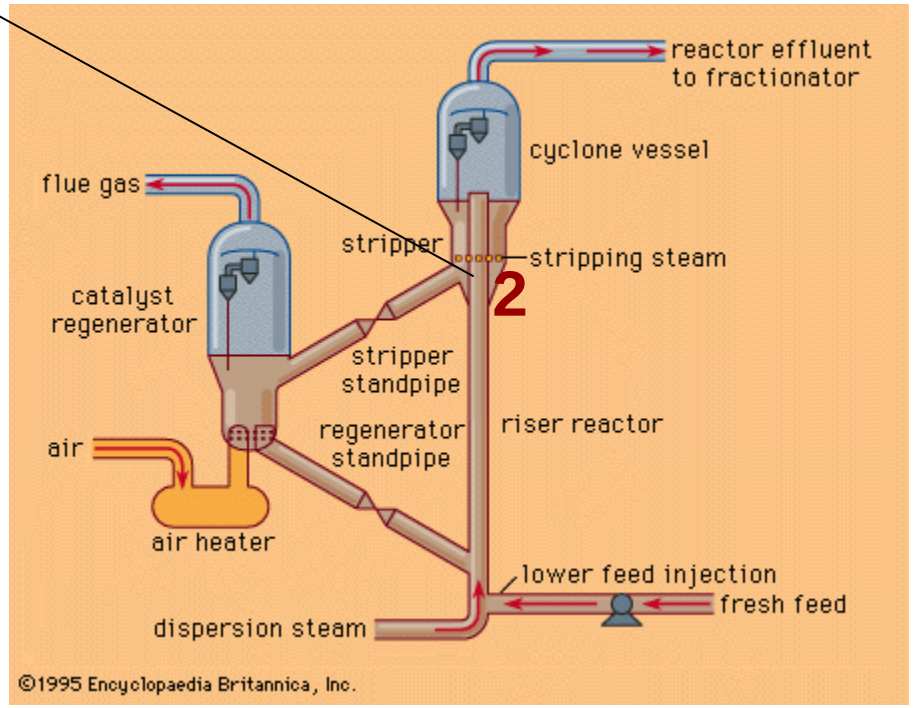
http://www.uyseg.org/catalysis/petrol/petrol2.htm

Fluidized Catalytic Cracking

- Different yields of products will occur depending on:
  - ***Temperature***
  - ***Inlet Feed Properties***

- Top of the riser, the catalyst separates from the mixture and is steam stripped

- The final product exits the top of the reactor

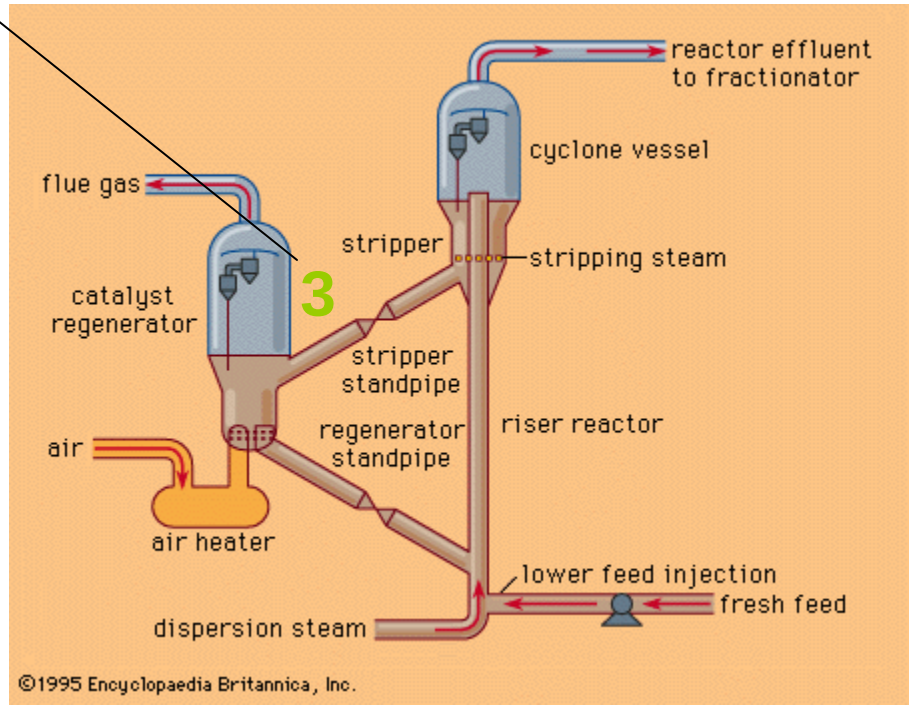


http://www.uyseg.org/catalysis/petrol/petrol2.htm

Fluidized Catalytic Cracking

• One product from catalytic cracking is "**coke**" or carbon that forms on the surface of the catalyst.

•To reactivate catalyst, it must be regenerated.

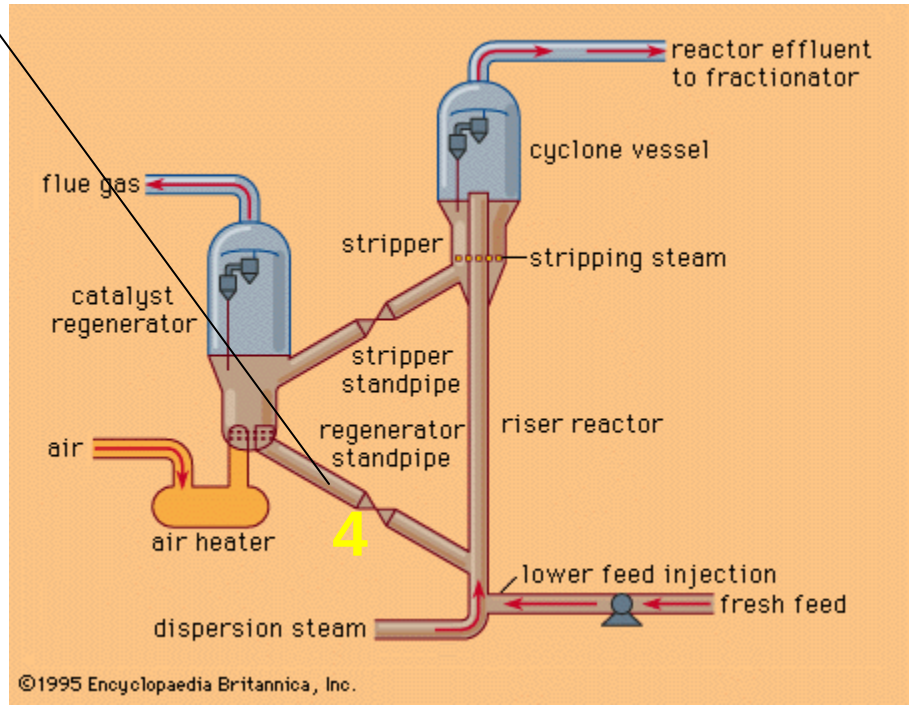


http://www.uyseg.org/catalysis/petrol/petrol2.htm

Fluidized Catalytic Cracking

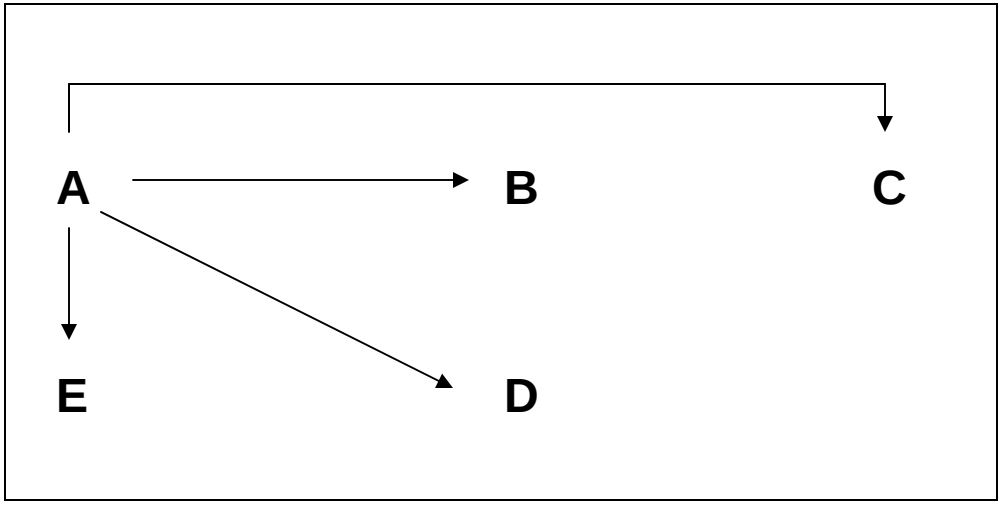
- Catalysis is **<u>regenerated</u>** by entering a combustion chamber and mixed with superheated air

- Energy released from regenerating the catalysis is then coupled with the inlet feed at the bottom of the riser
  - *Cracking*



http://www.uyseg.org/catalysis/petrol/petrol2.htm

Fluidized Catalytic Cracking



$A = gas\ oil$

$B = gasoline$

$C = LPG$

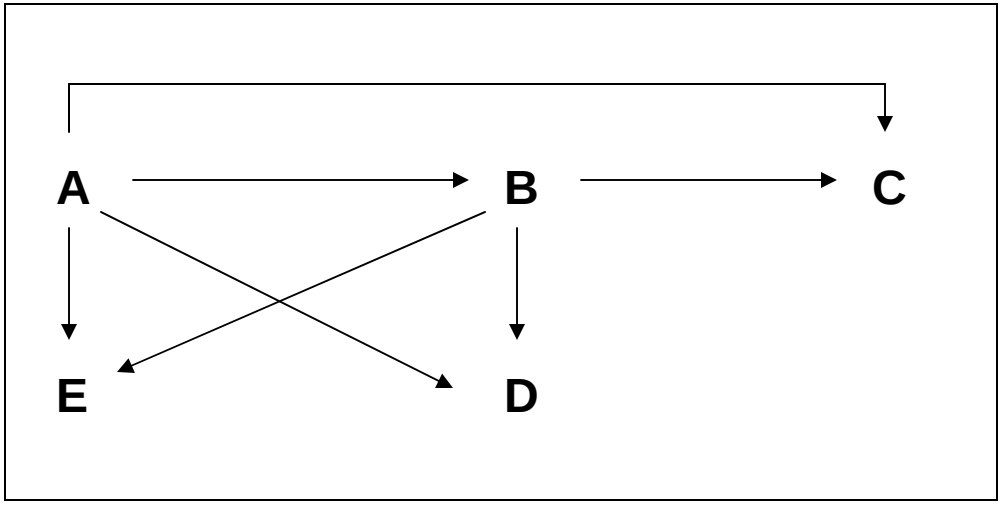
$D = dry\ gas$

$E = coke$

$$r_A = -(k_{A-B} + k_{A-C} + k_{A-D} + k_{A-E})\, y_A^2 \Phi$$

Ancheyta-Juarez, Jorge, “Estimation of Kinetic Constants….”, *Energy & Fuels,* **2000**, 14, 1226-1231

Fluidized Catalytic Cracking



$A = gas\ oil$

$B = gasoline$

$C = LPG$

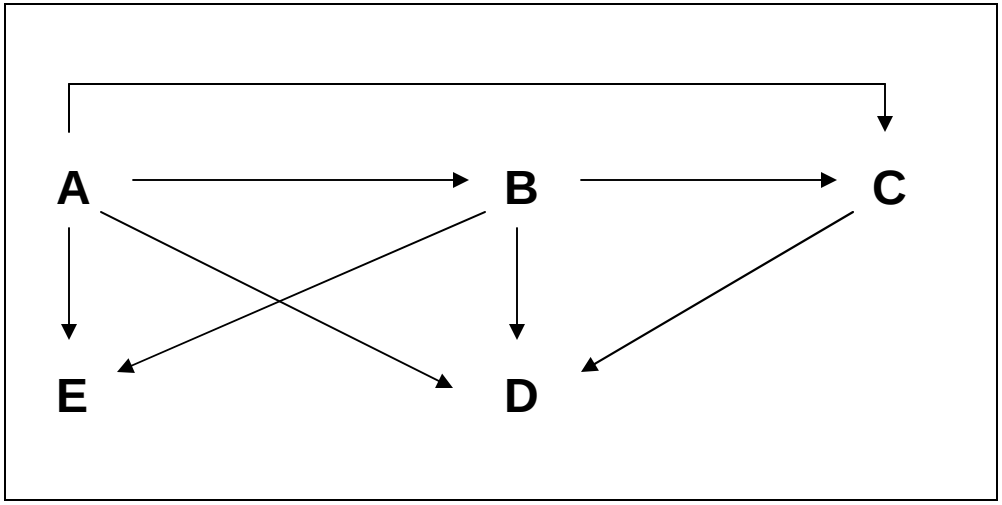
$D = dry\ gas$

$E = coke$

$$r_B = (k_{A-B} y_A^2 - k_{B-C} y_B - k_{B-D} y_B - k_{B-E} y_B)\Phi$$

Ancheyta-Juarez, Jorge, "Estimation of Kinetic Constants….", *Energy & Fuels,* **2000**, 14, 1226-1231

Fluidized Catalytic Cracking



$A = gas\ oil$

$B = gasoline$

$C = LPG$

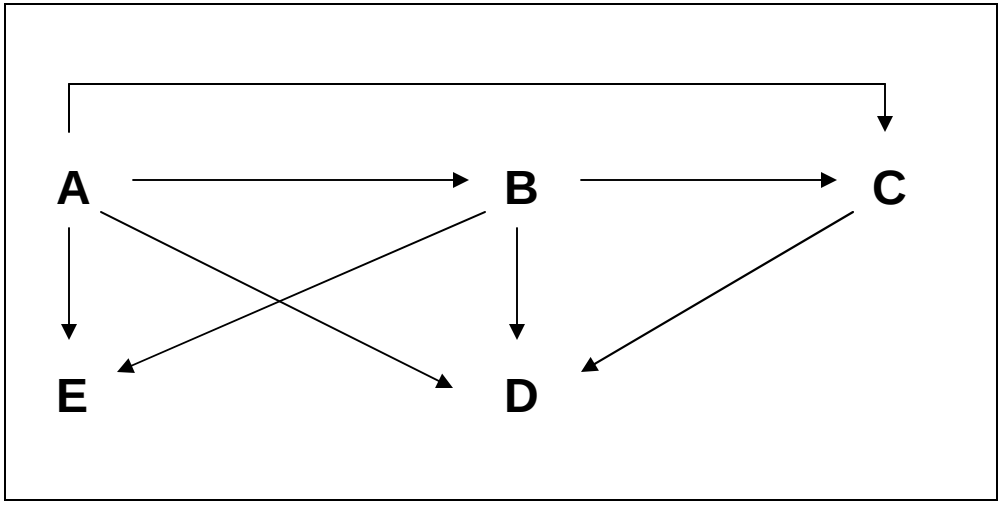
$D = dry\ gas$

$E = coke$

$$r_C = (k_{A-C} y_A^2 + k_{B-C} y_B - k_{C-D} y_C)\Phi$$

Ancheyta-Juarez, Jorge, "Estimation of Kinetic Constants….", *Energy & Fuels,* **2000**, 14, 1226-1231

Fluidized Catalytic Cracking



$A = gas\ oil$

$B = gasoline$

$C = LPG$

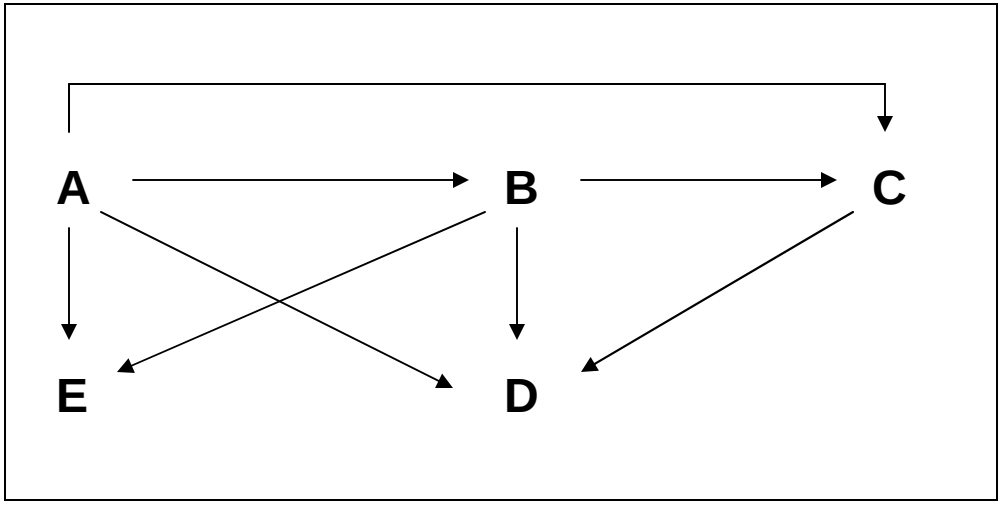
$D = dry\ gas$

$E = coke$

$$\Phi = e^{-k_d t_c}$$

Ancheyta-Juarez, Jorge, “Estimation of Kinetic Constants….”, *Energy & Fuels,* **2000**, 14, 1226-1231

Fluidized Catalytic Cracking



$A = gas\ oil$

$B = gasoline$

$C = LPG$

$D = dry\ gas$

$E = coke$

$$\Phi = e^{-k_d t_c}$$

- 8 kinetic constants
- One catalyst deactivation
- Gas Oil considered as a second order reaction

Ancheyta-Juarez, Jorge, “Estimation of Kinetic Constants….”, *Energy & Fuels,* **2000**, 14, 1226-1231

Fluidized Catalytic Cracking

- Assumptions
  - One-dimensional tubular reactor
    - No radial and axial dispersion
  - Cracking only takes place in the riser
  - Dispersion/Adsorption inside catalyst is negligible
  - Coke deposited does not affect the fluid flow

Fluidized Catalytic Cracking

- Change
  - Temperature
  - Inlet Feed

Kinetic Parameters for each Feedstock at 500 °C			
	A	B	C
k_d	1481.85	1785	1905.24
k_{ab}	3370.6	3171	2907.18
k_{ac}	510.88	491.74	477.02
k_{ad}	10.76	75.3	86.06
k_{ae}	390.03	442.96	540.67
k_{bc}	181.8	154.98	101.33
k_{bd}	20.89	25.46	29.38
k_{be}	0.75	0.915	1.06
k_{cd}	286.58	323.83	353.92

Mass Balance:

$$\frac{dy_i}{dz} = \frac{1}{WHSV}\left(\frac{\rho_L}{\rho_C}\right) * r_i$$

Fluidized Catalytic Cracking

- Change
  - Temperature
  - Inlet Feed

TEMPERATURE:
480, 500, 520 ºC

Kinetic Parameters for each Feedstock at 500 ºC

	A	B	C
k_d	1481.85	1785	1905.24
k_{ab}	3370.6	3171	2907.18
k_{ac}	510.88	491.74	477.02
k_{ad}	10.76	75.3	86.06
k_{ae}	390.03	442.96	540.67
k_{bc}	181.8	154.98	101.33
k_{bd}	20.89	25.46	29.38
k_{be}	0.75	0.915	1.06
k_{cd}	286.58	323.83	353.92

Mass Balance:

$$\frac{dy_i}{dz} = \frac{1}{WHSV}\left(\frac{\rho_L}{\rho_C}\right) * r_i$$

Fluidized Catalytic Cracking

- Constant C/O Ratio of 5
- Varying space velocity (WHSV)
  - 6 – 48 h^{-1}
- Gas Oil Conversion ~ 70 %
- Gasoline ~ 50%
- LPG ~ 12 %

Microsoft Excel - rate11111.xls

File Edit View Insert Format Tools Data Window Help

Arial 10 B I U

AF32

	Q	R	S	T	U	V	W	X	Y	Z	AA
1											
2		% YIELD		CONCENTRATIONS							
3		SUM	%	C_A	C_B	C_C	C_D	C_E			
4		1	0.00	1	0	0	0	0			
5		1	0.99	0.990129	0.007154	0.001174	0.000212	0.001331			
6		1	1.95	0.980453	0.014166	0.002326	0.000421	0.002635			
7		1	2.90	0.970964	0.021039	0.003456	0.000628	0.003914			
8		1	3.83	0.961658	0.027777	0.004564	0.000832	0.005169			
9		1	4.75	0.95253	0.034384	0.005653	0.001034	0.006399			
10		1	5.64	0.943574	0.040864	0.006722	0.001233	0.007606			
11		1	6.52	0.934786	0.047221	0.007771	0.001431	0.008791			
12		1	7.38	0.926161	0.053457	0.008802	0.001626	0.009954			
13		1	8.23	0.917694	0.059577	0.009815	0.001819	0.011095			
14		1	9.06	0.909381	0.065583	0.01081	0.00201	0.012216			
15		1	9.88	0.901218	0.071478	0.011787	0.0022	0.013317			
16		1	10.68	0.893202	0.077266	0.012748	0.002387	0.014398			
17		1	11.47	0.885327	0.082948	0.013693	0.002573	0.015459			
18		1	12.24	0.87759	0.088529	0.014622	0.002757	0.016502			
19		1	13.00	0.869988	0.09401	0.015536	0.002939	0.017527			
20		1	13.75	0.862517	0.099395	0.016434	0.003119	0.018535			
21		1	14.48	0.855174	0.104685	0.017318	0.003299	0.019525			
22		1	15.20	0.847955	0.109883	0.018187	0.003476	0.020498			
23		1	15.91	0.840858	0.114992	0.019043	0.003652	0.021455			
24		1	16.61	0.833879	0.120013	0.019885	0.003827	0.022396			
25		1	17.30	0.827015	0.124949	0.020714	0.004	0.023322			
26		1	17.97	0.820264	0.129802	0.02153	0.004172	0.024232			
27		1	18.64	0.813623	0.134573	0.022333	0.004343	0.025128			
28		1	19.29	0.807089	0.139266	0.023125	0.004512	0.026009			
29		1	19.93	0.800659	0.143881	0.023904	0.00468	0.026876			
30		1	20.57	0.794331	0.148421	0.024672	0.004847	0.027729			
31		1	21.19	0.788103	0.152887	0.025428	0.005013	0.028569			
32		1	21.80	0.781973	0.157281	0.026173	0.005178	0.029396			

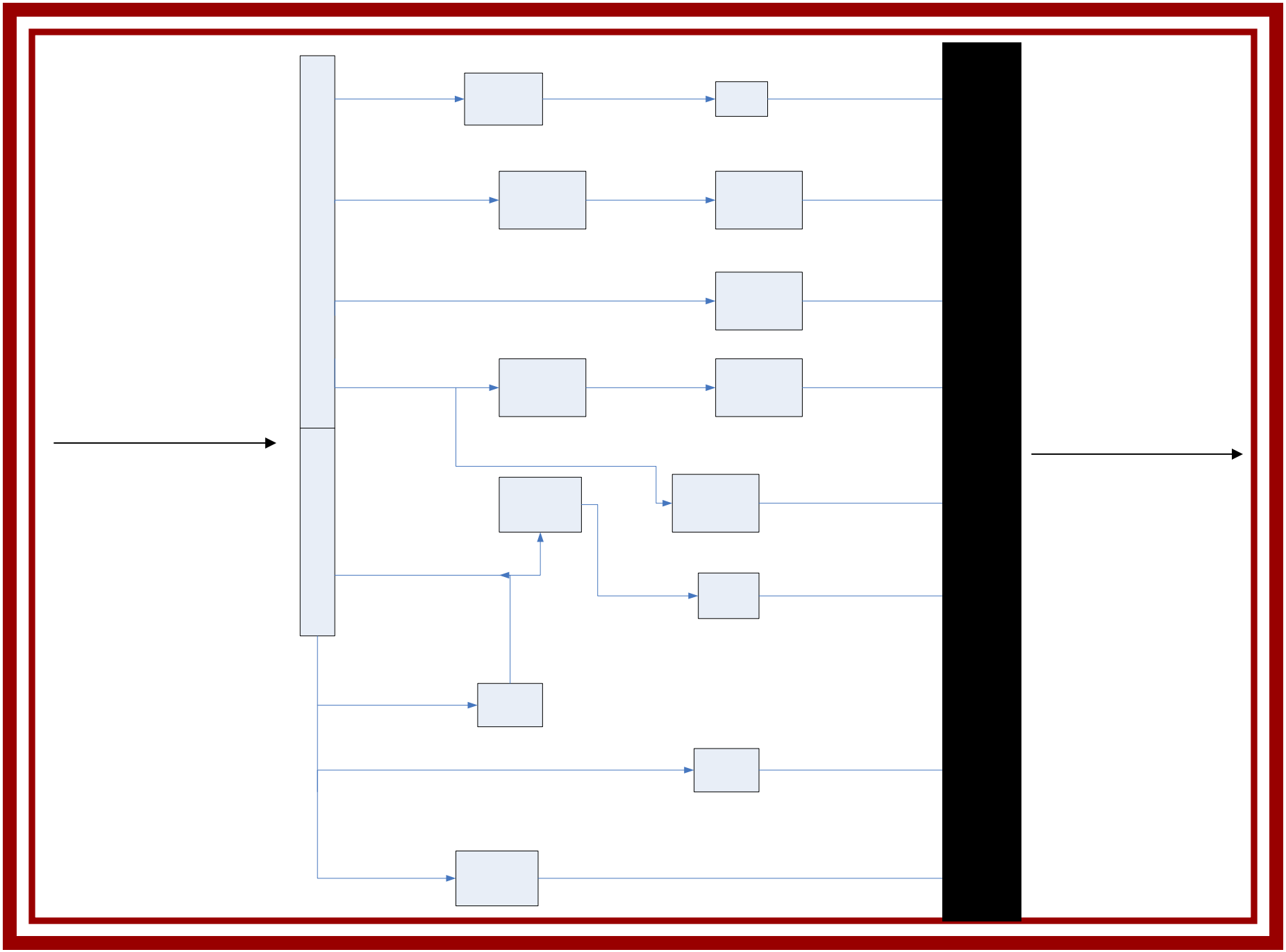
Microsoft Excel - rate11111.xls

File Edit View Insert Format Tools Data Window Help

Arial 10 B I U

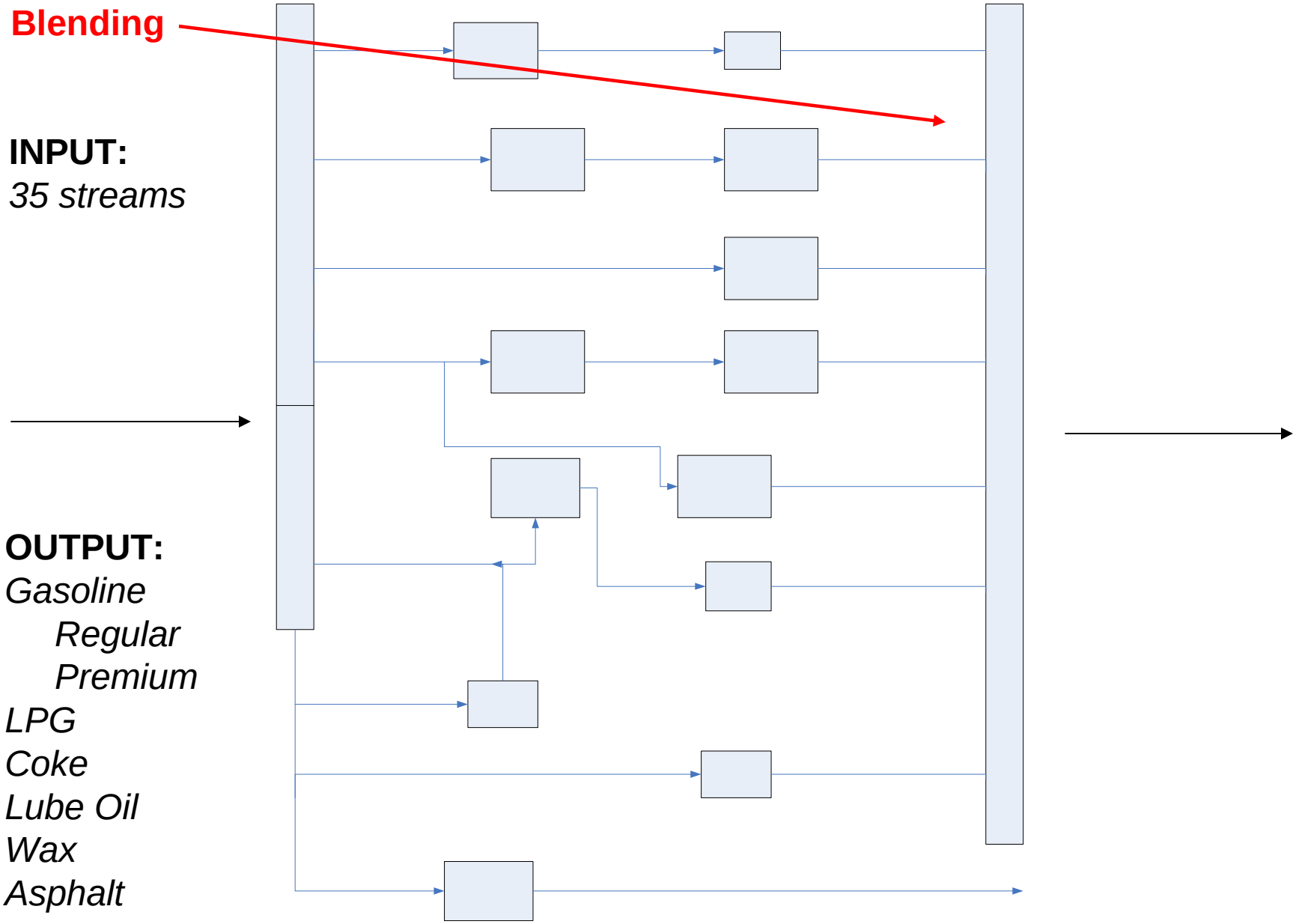
AF32

	Q	R	S	T	U	V	W	X	Y	Z	AA
1											
2		% YIELD		CONCENTRATIONS							
3		SUM	%	C_A	C_B	C_C	C_D	C_E			
4		1	0.00	1	0	0	0	0			
5		1	0.99	0.990129	0.007154	0.001174	0.000212	0.001331			
6		1	1.95	0.980453	0.014166	0.002326	0.000421	0.002635			
7		1	2.90	0.970964	0.021039	0.003456	0.000628	0.003914			
8		1	3.83	0.961658	0.027777	0.004564	0.000832	0.005169			
9		1	4.75	0.95253	0.034384	0.005653	0.001034	0.006399			
10		1	5.64	0.943574	0.040864	0.006722	0.001233	0.007606			
11		1	6.52	0.934786	0.047221	0.007771	0.001431	0.008791			
12		1	7.38	0.926161	0.053457	0.008802	0.001626	0.009954			
13		1	8.23	0.917694	0.059577	0.009815	0.001819	0.011095			
14		1	9.06	0.909381	0.065583	0.01081	0.00201	0.012216			
15		1	9.88	0.901218	0.071478	0.011787	0.0022	0.013317			
16		1	10.68	0.893202	0.077266	0.012748	0.002387	0.014398			
17		1	11.47	0.885327	0.082948	0.013693	0.002573	0.015459			
18		1	12.24	0.87759	0.088529	0.014622	0.002757	0.016502			
19		1	13.00	0.869988	0.09401	0.015536	0.002939	0.017527			
20		1	13.75	0.862517	0.099395	0.016434	0.003119	0.018535			
21		1	14.48	0.855174	0.104685	0.017318	0.003299	0.019525			
22		1	15.20	0.847955	0.109883	0.018187	0.003476	0.020498			
23		1	15.91	0.840858	0.114992	0.019043	0.003652	0.021455			
24		1	16.61	0.833879	0.120013	0.019885	0.003827	0.022396			
25		1	17.30	0.827015	0.124949	0.020714	0.004	0.023322			
26		1	17.97	0.820264	0.129802	0.02153	0.004172	0.024232			
27		1	18.64	0.813623	0.134573	0.022333	0.004343	0.025128			
28		1	19.29	0.807089	0.139266	0.023125	0.004512	0.026009			
29		1	19.93	0.800659	0.143881	0.023904	0.00468	0.026876			
30		1	20.57	0.794331	0.148421	0.024672	0.004847	0.027729			
31		1	21.19	0.788103	0.152887	0.025428	0.005013	0.028569			
32		1	21.80	0.781973	0.157281	0.026173	0.005178	0.029396			



Blending

INPUT:
35 streams



OUTPUT:
Gasoline
Regular
Premium
LPG
Coke
Lube Oil
Wax
Asphalt

Blending

- Final products are created by blending streams from refinery units
- 35 streams from 13 units are blended
- 30 streams are used in gasoline
- 5 streams are other products
  - Propane gas, lube oil, asphalt, wax, and coke

Blending Indexes

- Most properties do not blend linearly
- Empirical blending indexes are used to linearize the blending behavior

$$BI_{mix} = \sum_i x_i BI_i$$

Where BI is the Blending Index

x_i is the volume fraction of component i

Blending Indexes

Reid Vapor Pressure $$VPBI = \left(RVP\right)^{1.25}$$

Viscosity Index $$BI_v = \frac{\log_{10} \nu}{3 + \log_{10} \nu}$$

Pour Point $$BI_p = T_p^{\left(\frac{1}{0.08}\right)}$$

Cloud Point $$BI_{CL} = T_{CL}^{\left(\frac{1}{0.05}\right)}$$

Flash Point $$\log_{10} BI_F = -6.1188 + \frac{2414}{T_F - 42.6}$$

Aniline Point $$BI_{AP} = 1.124\left[\exp\left(0.00657AP\right)\right]$$

Gasoline Blending

- Specifications:
  - Octane (normal 87, premium 91)
  - Reid Vapor Pressure (EPA mandated)
  - Maximum additive amounts
- Inputs:
  - Market conditions (Price, Demand)
  - Incoming streams from refinery units
- Objective: Maximize Profit

Gasoline Blending

- Vapor pressure blending can be improved by using thermodynamically based methods
- Raoult's Law

$$P = \sum x_i P_i^*$$

Blending

- Other possible products
  - Fuel oils
  - Lube oils
  - Diesel fuel
- Blending requires data for aniline point, pour point, cloud point, flash point, and diesel index

Refinery Planning

- Addresses the planning of short-term crude oil purchasing and processing
- Does not address risk or uncertainty
- Determine purchasing schedule to meet:
  - Specification (Octane, n-Butane, etc.)
  - Demand with **HIGHEST** profit
- Decision Variables:
  - Crude oil purchase
  - Processing variables
    - Temperatures, Pressures, Blending mixtures

	On/Off	Name	Model	Flowrate [IN]	Input	Input	Output	Output	Flowrate	Variables	Variables
2	On	**Aaron**	*Hydrotreating*	5418.9	Aromatics (wt%)	0.107	Treated Non- Aromatics (wt%	0.89	4841.6	Temperature	370
3			Naptha		Nitrogen (wt %)	0.001	Treated Aromatics (wt%)	0.11	577.3	Pressure	344738
4					Sulfur (wt %)	0.010				Ratio Hyrdogen:Oil	200
5					Basic Nitrogen (wt%)	0.001					
6					MW	133					
7											
8			*Hydrotreating*	3852.4	Aromatics (wt%)	0.177	Treated Non- Aromatics (wt%	0.82	**3174.7**	Temperature	370
9			Middle Distillate		Nitrogen (wt %)	0.001	Treated Aromatics (wt%)	0.18	**677.7**	Pressure	344738
10					Sulfur (wt %)	0.020				Ratio Hyrdogen:Oil	200
11					Basic Nitrogen (wt%)	0.001					
12					MW	159					
13											
14			*Hydrotreating*	6559.9	Aromatics (wt%)	0.313	Treated Non- Aromatics (wt%	0.69	4509.7	Temperature	360
15			Heavy Atm. Gas Oil		Nitrogen (wt %)	0.018	Treated Aromatics (wt%)	0.31	2050.3	Pressure	344738
16					Sulfur (wt %)	0.085				Ratio Hyrdogen:Oil	200
17					Basic Nitrogen (wt%)	0.018					
18					MW	208					
19											
20	On		*Delayed Coking*	1155.1	Carbon Residue	29.1	Gas < C4 (wt%)	0.11	128.3	Pressure	35
21							Naptha (wt%)	0.19	214.9		
22							Gas Oil (wt%)	0.24	273.7		
23							Coke (wt%)	0.47	538.2		
24	Off	**Frow**	*Xylene Isomerization*		Aromatics (wt%)		Paraffins + Naptha (wt%)			Temperature	
25							Benzene (wt%)				
26							Toulene (wt%)				
27							Ethyl-Benzene (wt%)				
28							Ortho-Xylene (wt%)				
29							Para-Xylene (wt%)				
30											
31	On		*Solvent Extraction*	1155.1	Paraffin (wt %)	0.35	Paraffins (wt%)	99%	342.3	Temperature	125
32					Naptha (wt %)	0.1	Napthene +Aromatics (wt%)	1%	3.8	Solvent / Feed	2
33					Aromatic (wt %)	0.55	Aromatic (wt%)	92%	747.0		
34					API	24.0	Paraffins (wt%)	8%	62.0		
35											
36	On		*Catalytic Reforming*	5418.9	Paraffin (wt %)	0.45	Hydrogen (wt%)	1%	79.9	Temperature	950
37					Naptha (wt%)	0.45	Gas, C1-C4 (wt%)	8%	**452.0**	Pressure	35
38					Aromatic (wt%)	0.11	C5 + Reformate (wt%)	90%	**4887.0**	Recycle Rate	7.6
39					MW	133					
40					°API	52.2					
41	On	**Tom**	*Hydro Cracking*	500	°API	34.8	Light Naptha	0.19	**95.6**	Hydrogen/BBL	1000
42					Kw	11.8	Heavy Naptha	0.57	**285.1**		
43							C3 Up	0.05	**25.5**		
44							I-Butane	0.03	**14.1**		
45							n-Butane	0.03	**16.3**		
46							Gas Oil	0.13	**63.5**		
47											
48	On		*Solvent De'w'ax*	425	°API	26.3	Wax	0.36	**151.0**	Temperature	310
49							De-Wax	0.64	**274.0**		

Blend | Crude A | Crude B | Crude C | Crude Blend | Cat Crack Kinetic | Cat Crack | VisBreak | isomerization | HydroCrack | Solv. De

	On/Off	Name	Model	Flowrate [IN]	Input	Input	Output	Output	Flowrate	Variables	Variables
2	On	**Aaron**	*Hydrotreating*	5418.9	Aromatics (wt%)	0.107	Treated Non- Aromatics (wt%	0.89	4841.6	Temperature	370
3			Naptha		Nitrogen (wt %)	0.001	Treated Aromatics (wt%)	0.11	577.3	Pressure	344738
4					Sulfur (wt %)	0.010				Ratio Hyrdogen:Oil	200
5					Basic Nitrogen (wt%)	0.001					
6					MW	133					
7											
8			*Hydrotreating*	3852.4	Aromatics (wt%)	0.177	Treated Non- Aromatics (wt%	0.82	**3174.7**	Temperature	370
9			Middle Distillate		Nitrogen (wt %)	0.001	Treated Aromatics (wt%)	0.18	**677.7**	Pressure	344738
10					Sulfur (wt %)	0.020				Ratio Hyrdogen:Oil	200
11					Basic Nitrogen (wt%)	0.001					
12					MW	159					
13											
14			*Hydrotreating*	6559.9	Aromatics (wt%)	0.313	Treated Non- Aromatics (wt%	0.69	4509.7	Temperature	360
15			Heavy Atm. Gas Oil		Nitrogen (wt %)	0.018	Treated Aromatics (wt%)	0.31	2050.3	Pressure	344738
16					Sulfur (wt %)	0.085				Ratio Hyrdogen:Oil	200
17					Basic Nitrogen (wt%)	0.018					
18					MW	208					
19											
20	On		*Delayed Coking*	1155.1	Carbon Residue	29.1	Gas < C4 (wt%)	0.11	128.3	Pressure	35
21							Naptha (wt%)	0.19	214.9		
22							Gas Oil (wt%)	0.24	273.7		
23							Coke (wt%)	0.47	538.2		
24	Off	**Frow**	*Xylene Isomerization*		Aromatics (wt%)		Paraffins + Naptha (wt%)			Temperature	
25							Benzene (wt%)				
26							Toulene (wt%)				
27							Ethyl-Benzene (wt%)				
28							Ortho-Xylene (wt%)				
29							Para-Xylene (wt%)				
30											
31	On		*Solvent Extraction*	1155.1	Paraffin (wt %)	0.35	Paraffins (wt%)	99%	342.3	Temperature	125
32					Naptha (wt %)	0.1	Napthene +Aromatics (wt%)	1%	3.8	Solvent / Feed	2
33					Aromatic (wt %)	0.55	Aromatic (wt%)	92%	747.0		
34					API	24.0	Paraffins (wt%)	8%	62.0		
35											
36	On		*Catalytic Reforming*	5418.9	Paraffin (wt %)	0.45	Hydrogen (wt%)	1%	79.9	Temperature	950
37					Naptha (wt%)	0.45	Gas, C1-C4 (wt%)	8%	**452.0**	Pressure	35
38					Aromatic (wt%)	0.11	C5 + Reformate (wt%)	90%	**4887.0**	Recycle Rate	7.6
39					MW	133					
40					API	52.2					
41	On	**Tom**	*Hydro Cracking*	500	API	34.8	Light Naptha	0.19	**95.6**	Hydrogen/BBL	1000
42					Kw	11.8	Heavy Naptha	0.57	**285.1**		
43							C3 Up	0.05	**25.5**		
44							I-Butane	0.03	**14.1**		
45							n-Butane	0.03	**16.3**		
46							Gas Oil	0.13	**63.5**		
47											
48	On		*Solvent De'w'ax*	425	API	26.3	Wax	0.36	**151.0**	Temperature	310
49							De-Wax	0.64	**274.0**		

Blend | Crude A | Crude B | Crude C | Crude Blend | Cat Crack Kinetic | Cat Crack | VisBreak | isomerization | HydroCrack | Solv. De

	On/Off	Name	Model	Flowrate [IN]	Input	Input	Output	Output	Flowrate	Variables	Variables
2	On	**Aaron**	*Hydrotreating*	5418.9	Aromatics (wt%)	0.107	Treated Non- Aromatics (wt%	0.89	4841.6	Temperature	370
3			Naptha		Nitrogen (wt %)	0.001	Treated Aromatics (wt%)	0.11	577.3	Pressure	344738
4					Sulfur (wt %)	0.010				Ratio Hyrdogen:Oil	200
5					Basic Nitrogen (wt%)	0.001					
6					MW	133					
7											
8			*Hydrotreating*	3852.4	Aromatics (wt%)	0.177	Treated Non- Aromatics (wt%	0.82	**3174.7**	Temperature	370
9			Middle Distillate		Nitrogen (wt %)	0.001	Treated Aromatics (wt%)	0.18	**677.7**	Pressure	344738
10					Sulfur (wt %)	0.020				Ratio Hyrdogen:Oil	200
11					Basic Nitrogen (wt%)	0.001					
12					MW	159					
13											
14			*Hydrotreating*	6559.9	Aromatics (wt%)	0.313	Treated Non- Aromatics (wt%	0.69	4509.7	Temperature	360
15			Heavy Atm. Gas Oil		Nitrogen (wt %)	0.018	Treated Aromatics (wt%)	0.31	2050.3	Pressure	344738
16					Sulfur (wt %)	0.085				Ratio Hyrdogen:Oil	200
17					Basic Nitrogen (wt%)	0.018					
18					MW	208					
19											
20	On		*Delayed Coking*	1155.1	Carbon Residue	29.1	Gas < C4 (wt%)	0.11	128.3	Pressure	35
21							Naptha (wt%)	0.19	214.9		
22							Gas Oil (wt%)	0.24	273.7		
23							Coke (wt%)	0.47	538.2		
24	Off	**Frow**	*Xylene Isomerization*		Aromatics (wt%)		Paraffins + Naptha (wt%)			Temperature	
25							Benzene (wt%)				
26							Toulene (wt%)				
27							Ethyl-Benzene (wt%)				
28							Ortho-Xylene (wt%)				
29							Para-Xylene (wt%)				
30											
31	On		*Solvent Extraction*	1155.1	Paraffin (wt %)	0.35	Paraffins (wt%)	99%	342.3	Temperature	125
32					Naptha (wt %)	0.1	Napthene +Aromatics (wt%)	1%	3.8	Solvent / Feed	2
33					Aromatic (wt %)	0.55	Aromatic (wt%)	92%	747.0		
34					API	24.0	Paraffins (wt%)	8%	62.0		
35											
36	On		*Catalytic Reforming*	5418.9	Paraffin (wt %)	0.45	Hydrogen (wt%)	1%	79.9	Temperature	950
37					Naptha (wt%)	0.45	Gas, C1-C4 (wt%)	8%	**452.0**	Pressure	35
38					Aromatic (wt%)	0.11	C5 + Reformate (wt%)	90%	**4887.0**	Recycle Rate	7.6
39					MW	133					
40					°API	52.2					
41	On	**Tom**	*Hydro Cracking*	500	°API	34.8	Light Naptha	0.19	**95.6**	Hydrogen/BBL	1000
42					Kw	11.8	Heavy Naptha	0.57	**285.1**		
43							C3 Up	0.05	**25.5**		
44							I-Butane	0.03	**14.1**		
45							n-Butane	0.03	**16.3**		
46							Gas Oil	0.13	**63.5**		
47											
48	On		*Solvent De'w'ax*	425	°API	26.3	Wax	0.36	**151.0**	Temperature	310
49							De-Wax	0.64	**274.0**		

Blend | Crude A | Crude B | Crude C | Crude Blend | Cat Crack Kinetic | Cat Crack | VisBreak | isomerization | HydroCrack | Solv. De

	On/Off	Name	Model	Flowrate [IN]	Input	Input	Output	Output	Flowrate	Variables	Variables
2	On	**Aaron**	*Hydrotreating*	5418.9	Aromatics (wt%)	0.107	Treated Non- Aromatics (wt%	0.89	4841.6	Temperature	370
3			Naptha		Nitrogen (wt %)	0.001	Treated Aromatics (wt%)	0.11	577.3	Pressure	344738
4					Sulfur (wt %)	0.010				Ratio Hyrdogen:Oil	200
5					Basic Nitrogen (wt%)	0.001					
6					MW	133					
7											
8			*Hydrotreating*	3852.4	Aromatics (wt%)	0.177	Treated Non- Aromatics (wt%	0.82	**3174.7**	Temperature	370
9			Middle Distillate		Nitrogen (wt %)	0.001	Treated Aromatics (wt%)	0.18	**677.7**	Pressure	344738
10					Sulfur (wt %)	0.020				Ratio Hyrdogen:Oil	200
11					Basic Nitrogen (wt%)	0.001					
12					MW	159					
13											
14			*Hydrotreating*	6559.9	Aromatics (wt%)	0.313	Treated Non- Aromatics (wt%	0.69	4509.7	Temperature	360
15			Heavy Atm. Gas Oil		Nitrogen (wt %)	0.018	Treated Aromatics (wt%)	0.31	2050.3	Pressure	344738
16					Sulfur (wt %)	0.085				Ratio Hyrdogen:Oil	200
17					Basic Nitrogen (wt%)	0.018					
18					MW	208					
19											
20	On		*Delayed Coking*	1155.1	Carbon Residue	29.1	Gas < C4 (wt%)	0.11	128.3	Pressure	35
21							Naptha (wt%)	0.19	214.9		
22							Gas Oil (wt%)	0.24	273.7		
23							Coke (wt%)	0.47	538.2		
24	Off	**Frow**	*Xylene Isomerization*		Aromatics (wt%)		Paraffins + Naptha (wt%)			Temperature	
25							Benzene (wt%)				
26							Toulene (wt%)				
27							Ethyl-Benzene (wt%)				
28							Ortho-Xylene (wt%)				
29							Para-Xylene (wt%)				
30											
31	On		*Solvent Extraction*	1155.1	Paraffin (wt %)	0.35	Paraffins (wt%)	99%	342.3	Temperature	125
32					Naptha (wt %)	0.1	Napthene +Aromatics (wt%)	1%	3.8	Solvent / Feed	2
33					Aromatic (wt %)	0.55	Aromatic (wt%)	92%	747.0		
34					API	24.0	Paraffins (wt%)	8%	62.0		
35											
36	On		*Catalytic Reforming*	5418.9	Paraffin (wt %)	0.45	Hydrogen (wt%)	1%	79.9	Temperature	950
37					Naptha (wt%)	0.45	Gas, C1-C4 (wt%)	8%	**452.0**	Pressure	35
38					Aromatic (wt%)	0.11	C5 + Reformate (wt%)	90%	**4887.0**	Recycle Rate	7.6
39					MW	133					
40					°API	52.2					
41	On	**Tom**	*Hydro Cracking*	500	°API	34.8	Light Naptha	0.19	**95.6**	Hydrogen/BBL	1000
42					Kw	11.8	Heavy Naptha	0.57	**285.1**		
43							C3 Up	0.05	**25.5**		
44							I-Butane	0.03	**14.1**		
45							n-Butane	0.03	**16.3**		
46							Gas Oil	0.13	**63.5**		
47											
48	On		*Solvent De'w'ax*	425	°API	26.3	Wax	0.36	**151.0**	Temperature	310
49							De-Wax	0.64	**274.0**		

Blend | Crude A | Crude B | Crude C | Crude Blend | Cat Crack Kinetic | Cat Crack | VisBreak | isomerization | HydroCrack | Solv. De

Refinery Planning

- **Max Profit**

Pongsakdi, Arkadej, et. al, “Financial risk….”, *Int. J. Production Economics*, **accepted** 20 April 2005

$$= \sum_{t \in T} \sum_{c \in C_p} MANU_{c,t} * cp_{c,t} - \sum_{t \in T} \sum_{c \in C_o} AC_{c,t} * co_{c,t} - \sum_{t \in T} \sum_{c \in C_p} AL_{c,t} * cl_{c,t}$$

Refinery Planning

- **Max Profit**

Pongsakdi, Arkadej, et. al, “Financial risk….”, *Int. J. Production Economics*, **accepted** 20 April 2005

Product Sales

$$= \sum_{t \in T} \sum_{c \in C_p} MANU_{c,t} * cp_{c,t} - \sum_{t \in T} \sum_{c \in C_o} AC_{c,t} * co_{c,t} - \sum_{t \in T} \sum_{c \in C_p} AL_{c,t} * cl_{c,t}$$

Amount of product produced in that time period *multiplied* by unit sale price of product c

Refinery Planning

- **Max Profit**

Pongsakdi, Arkadej, et. al, “Financial risk….”, *Int. J. Production Economics*, **accepted** 20 April 2005

Product Sales **Crude Oil Costs**

$$= \sum_{t \in T} \sum_{c \in C_p} MANU_{c,t} * cp_{c,t} - \sum_{t \in T} \sum_{c \in C_o} AC_{c,t} * co_{c,t} - \sum_{t \in T} \sum_{c \in C_p} AL_{c,t} * cl_{c,t}$$

Amount of product produced in that time period *multiplied* by unit sale price of product c

Amount of crude oil refined in that time period *multiplied* by unit purchase price of crude oil

Refinery Planning

- **Max Profit**

Pongsakdi, Arkadej, et. al, “Financial risk….”, *Int. J. Production Economics*, **accepted** 20 April 2005

Product Sales **Crude Oil Costs** **Discounted Expense**

$$= \sum_{t \in T} \sum_{c \in C_p} MANU_{c,t} * cp_{c,t} - \sum_{t \in T} \sum_{c \in C_o} AC_{c,t} * co_{c,t} - \sum_{t \in T} \sum_{c \in C_p} AL_{c,t} * cl_{c,t}$$

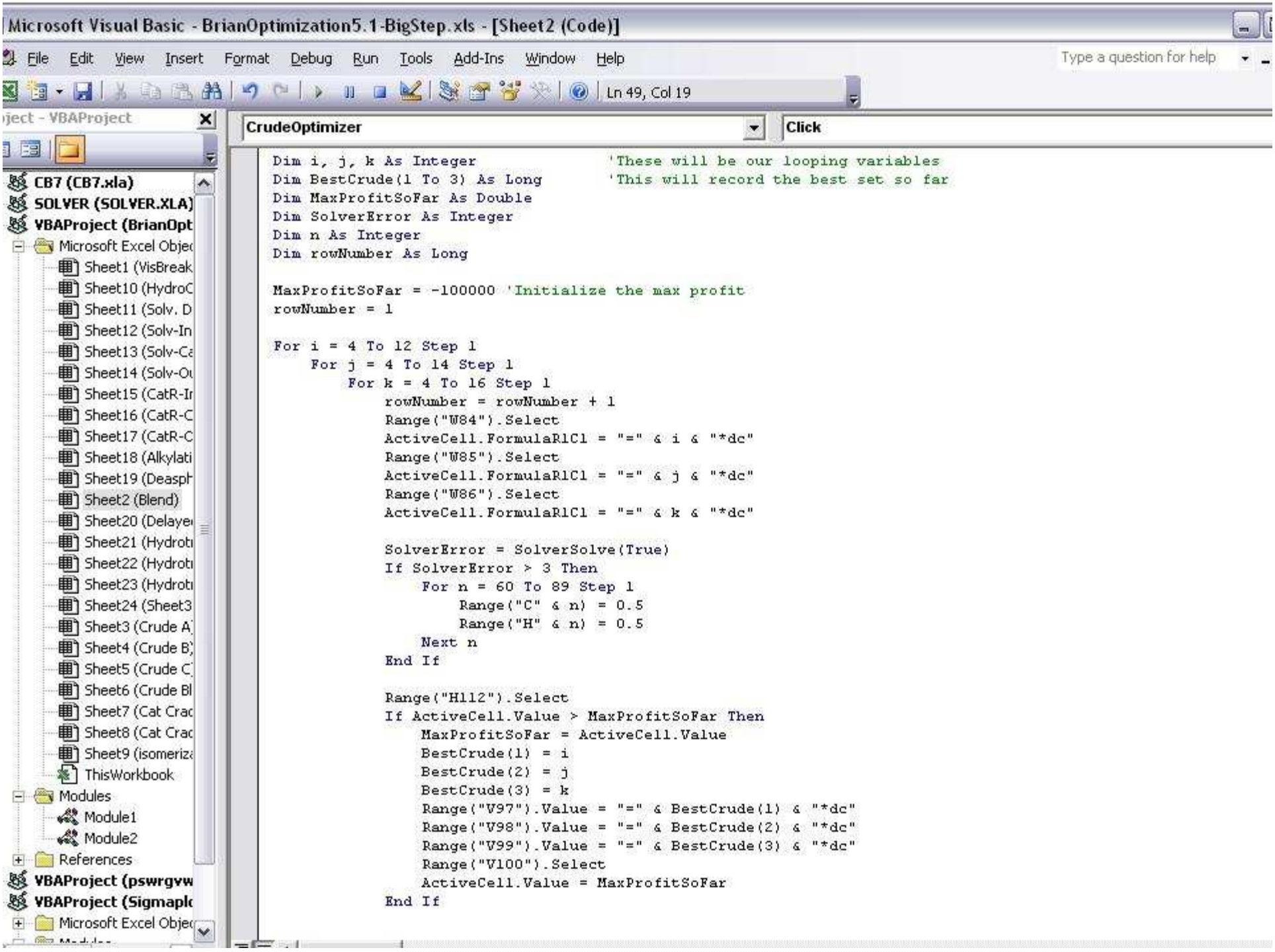
Amount of product produced in that time period *multiplied* by unit sale price of product c

Amount of crude oil refined in that time period *multiplied* by unit purchase price of crude oil

Amount of product volume that cannot satisfy demand *multiplied* by discounted price

Modeling

- A Visual Basic macro in Excel was used to help Solver find the optimal crude selection


Microsoft Visual Basic - BrianOptimization5.1-BigStep.xls - [Sheet2 (Code)]
File Edit View Insert Format Debug Run Tools Add-Ins Window Help
Type a question for help
Ln 49, Col 19
CrudeOptimizer
Click
CB7 (CB7.xla)
SOLVER (SOLVER.XLA)
VBAProject (BrianOpt
Microsoft Excel Objec
Sheet1 (VisBreak
Sheet10 (HydroC
Sheet11 (Solv. D
Sheet12 (Solv-In
Sheet13 (Solv-Ca
Sheet14 (Solv-Ou
Sheet15 (CatR-In
Sheet16 (CatR-C
Sheet17 (CatR-C
Sheet18 (Alkylati
Sheet19 (Deasph
Sheet2 (Blend)
Sheet20 (Delaye
Sheet21 (Hydrot
Sheet22 (Hydrot
Sheet23 (Hydrot
Sheet24 (Sheet3
Sheet3 (Crude A
Sheet4 (Crude B
Sheet5 (Crude C
Sheet6 (Crude Bl
Sheet7 (Cat Crac
Sheet8 (Cat Crac
Sheet9 (isomeriz
ThisWorkbook
Modules
Module1
Module2
References
VBAProject (pswrgvw
VBAProject (Sigmaplc
Microsoft Excel Objec
Dim i, j, k As Integer 'These will be our looping variables
Dim BestCrude(1 To 3) As Long 'This will record the best set so far
Dim MaxProfitSoFar As Double
Dim SolverError As Integer
Dim n As Integer
Dim rowNumber As Long
MaxProfitSoFar = -100000 'Initialize the max profit
rowNumber = 1
For i = 4 To 12 Step 1
For j = 4 To 14 Step 1
For k = 4 To 16 Step 1
rowNumber = rowNumber + 1
Range("W84").Select
ActiveCell.FormulaR1C1 = "=" & i & "*dc"
Range("W85").Select
ActiveCell.FormulaR1C1 = "=" & j & "*dc"
Range("W86").Select
ActiveCell.FormulaR1C1 = "=" & k & "*dc"
SolverError = SolverSolve(True)
If SolverError > 3 Then
For n = 60 To 89 Step 1
Range("C" & n) = 0.5
Range("H" & n) = 0.5
Next n
End If
Range("H112").Select
If ActiveCell.Value > MaxProfitSoFar Then
MaxProfitSoFar = ActiveCell.Value
BestCrude(1) = i
BestCrude(2) = j
BestCrude(3) = k
Range("V97").Value = "=" & BestCrude(1) & "*dc"
Range("V98").Value = "=" & BestCrude(2) & "*dc"
Range("V99").Value = "=" & BestCrude(3) & "*dc"
Range("V100").Select
ActiveCell.Value = MaxProfitSoFar
End If

Model Inputs

- Inputs:
  - Crude A: $71.88 / barrel (Australia)
  - Crude B: $72.00 / barrel (Kazakhstan)
  - Crude C: $71.20 / barrel (Saudi Arabia)
  - Regular Gasoline:
    - $2.75 / gal ($2.12)
    - Demand: 310,000 bbl/month
  - Premium Gasoline:
    - $3.00 / gal ($2.31)
    - Demand: 124,000 bbl/month

Energy Information Administration, U.S. Department of Energy
http://www.eia.doe.gov/oil_gas/petroleum/info_glance/petroleum.html

Model Results

- Outputs:
  - Maximum Profit: $21 per barrel
  - Crude Selection:
    - Crude A: 150,000 bbl/month
    - Crude B: 150,000 bbl/month
    - Crude C: 300,000 bbl/month
  - Demand exactly met

Future Work

- Include storage of crude and products
- Include risk and uncertainty
- Demand changing over time
- Wider variety of products: diesel, solvents, fuel oils, lube oils, etc.

Questions?