Process Optimization of Coal to Natural Gas Liquids via Fischer-Tropsch Gasification

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Abstract

Coal along with Shale Gas and Crude oil remains the major source of energy and feed stock for the foreseeable future. Coal reserves are approximately 20 times more than the crude oil reserves and hence there is a growing interest in coal gasification to liquid fuels via the Fisher-Tropsch technology. In this work, the process of converting coal to natural gas liquids is studied and the mass targets are obtained for fractions C2-C3 and methanol. The optimum composition of the syngas derived from the coal gasification is calculated for each of the component. Also, a general framework is developed to produce C1-C3 hydrocarbons from syngas derived from coal gasification. The insights obtained from this model, can be used to investigate possible technologies and the energy trade offs of the different technologies. Suitable product portfolio can be suggested for a given composition of coal.

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Introduction

Gas to Liquid Fuel plants have attracted tremendous attention recently due to the abundance of Shale Gas in the US. Shale gas can be converted into useful synthetic liquid fuels via the Fisher-Tropsch reaction. The syngas route is especially favorable due to the low sulfur content of the liquid fuels. Coal, is one of the promising alternative to shale gasification and can be used as a feed stock to produce hydrogen, methanol and other chemicals. There is a lot of interest in using coal, biomass to convert it to liquid fuel to displace part of the energy consumption by the transport sector.[1] The state of the art approach that researchers undertake is the optimization of a hybrid of coal and biomass feedstock to produce liquid fuels.[2]

Coal is an attractive feedstock that can be used to produce synthetic liquid fuels and thus attention has shifted towards coal gasification to produce liquid fuels in countries that have very large coal reserves.[3] Coal is burned for fuel and electricity production, but there is growing interest in countries like China, South Africa and India to produce large Coal to Liquid Fuel facilities to reduce dependence on oil from imports by producing a part of synthetic lubricants and fuels[4] and thereby reduce the dependence on imported crude oil as the major energy source.

The Fisher-Tropsch synthesis is the main process that will be used to produce syngas from Coal and convert it into liquid fuels. This case study, will be restricted to optimization of Coal gas to Ethane, Propane isomers and Methanol. Ethane, Propane and Butane are part of the hydrocarbon system referred to as **Natural Gas Liquids**, which is a versatile feed stock that can be manipulated to a variety of products. According to the Energy Information Agency,[5] the ethane market is currently the largest. Coal is attractive due to its relatively cheap cost ($2-$2.5/MM Btu) compared to Natural Gas ($4.8-$5.8/MM Btu).[6] When mixed with solid waste or other biomass, the option of coal gasification is both economically and environmentally desirable.[7]

Problem Statement

The deliverables of this study will be as follows

1. Targeting the maximum yield of Ethane, Propane and Butane from coal.
2. Optimization of conditions necessary for each of the product from feed.
3. Optimization of Coal Selection and thereby, the coal gas composition.

These specific problems will be formulated into a mathematical programming problem and will be solved using LINGO®.

Model Description

The Chemical potential μ is defined as

$$\mu_i = \Delta G_{f_i}^o + \mathrm{RT}\ ln(\frac{y_i \hat{\phi}_i P}{P^o}) \tag{1}$$

Assuming that all the species involved are ideal gas, at 1 bar and $T \geq 273.15K$ the following equation maybe applied, to minimize the gibbs free energy for a given set of equilibrium reactions. The reaction enthalpies are mentioned next to the

$$\frac{\Delta {G_{fi}}^o}{RT} + ln\frac{n_i}{\sum_k n_i} + \sum_k \frac{\lambda_k}{\mathrm{R}T} a_{ik} = 0 \tag{2}$$

The $\Delta {G_f}^o$ data of the species were taken from the Handbook of Chemistry and Physics[8] and were fit to a quadratic equation to model the change of $\Delta {G_f}^o$ with respect to temperature.

The model that was developed, used a set of equilibrium reactions and the total Gibbs free energy was minimized for a set of objectives (temperature, specific product

yields). This model gives an estimate of the outlet composition given a set of reactions. For the input, 3 streams are considered namely Carbon Monoxide, Carbon Dioxide and Steam.

The optimization model was run to simulate the equilibrium product distribution for the following conditions

- For a given composition of Coal, the operating conditions to obtain syngas.
- The process conditions of the reformer for maximizing the equilibrium composition of a particular component.
- The equilibrium composition of the products for a given feed ratio.

Reaction Models

The following reactions are considered as the possible reactions that take place in the reformer and the coal gasifier.

$C + H_2O \rightleftharpoons CO + H_2$	ΔH^o = -152kJ/mol
$CO + H_2O \rightleftharpoons CO_2 + H_2$	ΔH^o = -41 kJ/mol
$C + CO_2 \rightleftharpoons 2\,CO$	ΔH^o = 172kJ/mol
$nCO + (2\,n + 1\,)H_2 \rightleftharpoons C_nH_{2n+2} + nH_2O$	ΔH^o = -167kJ/mol/CO
$nCO + (2\,n^{+}2)H_2 \rightleftharpoons C_nH_{2n} + nH_2O$	ΔH^o = -167kJ/mol/CO
$nCO + 2\,nH_2 \rightleftharpoons C_nH_{2n+1}OH + (n-1)H_2O$	ΔH^o = -72kJ/mol/CO

The Model variables to be optimized are as follows

- Temperature 300-1500 K
- Inlet stream concentration (Steam and Carbon Dioxide)

The constraints placed on the model were as follows

- Steam concentration $\leq$ 5 times the inlet carbon concentration (Coal)
- Carbon Dioxide concentration $\leq$ 2 times the inlet carbon concentration (Coal)

- Mass balance of atomic entities (Inlet carbon, hydrogen and oxygen atoms are equal to output streams)
- Energy Input and Output depends on the Enthalpies of the components (i.e No Energy Loss)

Results

The mass targets can be obtained by 2 possible methods, these are

- The possible syngas composition from the given coal composition
- The syngas composition required for each of the componments obtained stoichiometrically

The results from both the approaches are discussed below.

Syngas ratios for each component

From the reaction stoichiometry, the syngas ratio (CO : H_2) required are tabulated below. The underlying assumption is that the selectivity of the product is 100% and hence represent the best case scenarios. Later these numbers will be used to analyze the equilibrium composition of the products at different temperatures.

Table I: The mass targets for each components obtained from stoichiometry

Component	Ratio of $H_2 : CO$
CH_4	3
C_2H_6	2.5
C_2H_4	1.5
C_3H_6	1.5
C_3H_8	2.34
CH_3OH	2

Syngas ratios obtained from a given coal composition

For the sake of simplicity, the following coal compositions were considered for the gasification due to the availability of data and its common usage. An equilibrium model was developed to investigate the composition of the outlet. The coal composition considered

- Illinois No-6 Bituminous Coal[7]
- Pittsburg No-8 Coal[9]

The composition data were obtained from literature are tabulated below,

Table II: The composition data on (reported in % dry basis)

Component	Illinois #6	Pittsburg #8
C	80.23	77.2
H	5.42	5.2
O	9.06	5.9
N	1.58	1.19
S	3.6	2.6
Ash	11.4	7.9
HHV (kJ/g)	27.114	31.8

Reformer Modeling

The optimization code is run at different temperature using a constant steam ratio to determine the equilibrium concentration. These are tabulated as follows

Temperature 500K

Table III: The equilibrium composition in the Reformer at 500K

Variable	Value
T	500
X	0
Y	1
Z	1
NINC	1
NINCO2	1
NINH2O	1
NCH4	$0.2201544 * 10^{-1}$
NCO	$0.9040899 * 10^{-4}$
NCO2	1.977876
NC2H6	$0.1736623 * 10^{-7}$
NC2H4	$0.8960651 * 10^{-5}$
NC3H6	$0.1469688 * 10^{-8}$
NC3H8	0
NH2O	0.9498516
H_{OUT}	-986.2812
H_{IN}	-821.5048
E_{INPUT}	-164.7764

Temperature 750K

Table IV: The equilibrium composition in the Reformer at 750K

Variable	Value
T	750
X	0
Y	1
Z	1
NINC	1
NINCO2	1
NINH2O	1
NCH4	$0.4879889 * 10^{-1}$
NCO	$0.9623470 * 10^{-1}$
NCO2	1.815392
NC2H6	$0.1182601 * 10^{-2}$
NC2H4	$0.1663232 * 10^{-1}$
NC3H8	$0.8766293 * 10^{-4}$
NC3H6	$0.1227132 * 10^{-2}$
NH2O	0.6488497
NH2	0.2127080
H_{OUT}	-986.2812
H_{IN}	-821.5048
E_{INPUT}	-164.7764

Temperature 1000K

Table V: The equilibrium composition in the Reformer at 1000K

Variable	Value
T	1000
X	0
Y	1
Z	1
NINC	1
NINCO2	1
NINH2O	1
NCH4	$0.5117639 * 10^{-2}$
NCO	1.179757
NCO2	0.7637956
NC2H6	$0.3994752 * 10^{-2}$
NC2H4	$0.1895940 * 10^{-1}$
NC3H8	$0.3135840 * 10^{-3}$
NC3H6	$0.1493485 * 10^{-2}$
NH2O	0.6488497
NH2	0.2127080
H_{OUT}	-429.7009
H_{IN}	-679.3400
E_{INPUT}	249.6391

Temperature 1250K

Table VI: The equilibrium composition in the Reformer at 1250K

Variable	Value
T	1250
X	0
Y	1
Z	1
NINC	1
NINCO2	1
NINH2O	1
NCH4	$0.1457321 * 10^{-4}$
NCO	1.402912
NCO2	0.5970406
NC2H6	$0.2638985 * 10^{-5}$
NC2H4	$0.1384036 * 10^{-4}$
NC3H8	$0.5520419 * 10^{-8}$
NC3H6	$0.2919904E * 10^{-7}$
NH2O	0.4030071
NH2	0.5969281
H_{OUT}	-386.1235
H_{IN}	-679.3400
E_{INPUT}	293.2165

Temperature 1500K

Table VII: The equilibrium composition in the Reformer at 1500K

Variable	Value
T	1500
X	0
Y	1
Z	1
NINC	1
NINCO2	1
NINH2O	1
NCO	1.476488
NCO2	0.5235116
NCH4	$0.2072866 * 10^{-6}$
NC2H6	$0.1320318 * 10^{-7}$
NC2H4	$0.7877977 * 10^{-7}$
NC3H8	0
NC3H6	0
NH2O	0.4764888
NH2	0.5235106
H_{OUT}	-353.4078
H_{IN}	-679.3400
E_{INPUT}	325.9322

Optimum Equilibrium Composition

The results from the LINGO® are tabulated below. The program algorithm is similar to the formulation by Noureldin et al.[10] Each component of industrial significance is optimized to get the maximum yield for an input of 1 mol of Carbon(Coal).

Syngas

The syngas composition of 1:2 is important in producing synthetic fuels and methanol.

The results obtained are as follows

Table VIII: The process conditions for producing syngas of composition CO:$H_2 inratio 1:2$

Variable	Value
T	1342.127
X	0
Y	0.4488999
Z	0.2608135
NINC	1
NINCO2	0.2608135
NINH2O	0.4488999
NCH4	$0.3210443 * 10^{-3}$
NCO	1.096456
NCO2	$0.2645235 * 10^{-2}$
NCH4	$0.2645235 * 10^{-2}$
NC2H6	$0.2645235 * 10^{-2}$
NC2H4	$0.5326038 * 10^{-1}$
NC3H6	$0.1004598 * 10^{-1}$
NC3H8	$0.1804116 * 10^{-2}$
NH2O	$0.1289074 * 10^{-2}$
H_{OUT}	-77.78127
H_{IN}	-240.8270
E_{INPUT}	163.0457

Hydrogen rich Syngas

Hydrogen rich syngas are used in metallurgical applications and as feed stock for synthetic hydrocarbon fuels. Typically hydrogen rich syngas has a CO:$H_2 ratio of$1:4

Table IX: The process conditions for producing syngas of composition CO:$H_2 in ratio$1 : 2

Variable	Value
T	975
NINC	1
NINCO2	0
NINH2O	3.092609
NCH4	$0.3210443 * 10^{-3}$
NCO	0.3919079
NH2	1.567632
NCO2	$0.2645235 * 10^{-2}$
NCH4	$0.48807 * 10^{-2}$
NC2H6	$0.867541 * 10^{-3}$
NC2H4	$0.5326038 * 10^{-1}$
NC3H6	$0.5539485 * 10^{-4}$
NC3H8	$0.2030048 * 10^{-4}$
NH2O	1.507645
H_{OUT}	-547.1724
H_{IN}	-883.9604
E_{INPUT}	336.7880

Hydrogen

The process of producing hydrogen in this model revolves around generating syngas and using the water gas shift to increase the hydrogen concentration. The results obtained are below

Table X: The process conditions for producing maximum Hydrogen

Variable	Value
T	907.7814
X	0
Y	5
Z	0
NINC	1
NINCO2	0
NINH2O	5
NCH4	$0.58723668 * 10^{-2}$
NCO	0.1988723
NCO2	0.7931388
NC2H6	$0.2289840 * 10^{-3}$
NC2H4	$0.8116182 * 10^{-3}$
NC3H6	$0.2589619 * 10^{-5}$
NC3H8	$0.9187669 * 10^{-5}$
NH2O	3.214850
NH2	1.771057
H_{OUT}	-983.02991
H_{IN}	-1429.150
E_{INPUT}	446.1201

Methane

The gasification of coal to produce methane directly can be useful in some applications to produce synthetic coal gas

Table XI: The process conditions for producing maximum methane

Variable	Value
T	1342.127
X	0
Y	2.001064
Z	0.2608135
NINC	1
NINCO2	0.2608135
NINH2O	0.4488999
NCH4	$0.3210443 * 10^{-3}$
NCO	1.096456
NCO2	$0.2645235 * 10^{-2}$
NCH4	$0.2645235 * 10^{-2}$
NC2H6	$0.2645235 * 10^{-2}$
NC2H4	$0.5326038 * 10^{-1}$
NC3H6	$0.1004598 * 10^{-1}$
NC3H8	$0.1804116 * 10^{-2}$
NH2O	$0.1289074 * 10^{-2}$
H_{OUT}	-77.78127
H_{IN}	-240.8270
E_{INPUT}	163.0457

Ethane

Table XII: The process conditions for producing maximum Ethane

Variable	Value
T	914.0579
X	0
Y	1.107026
Z	0
NINC	1
NINCO2	0
NINH2O	1.107026
NCH4	0.0307924
NCO	0.3052146
NCO2	0.2993268
NC2H6	0.02960754
NC2H4	0.1018332
NC3H6	$0.2629258 * 10^{-1}$
NC3H8	$0.7635581 * 10^{-2}$
NH2O	0.2031581
NH2	0.4403743
H_{OUT}	-175.2597
H_{IN}	-316.4214
E_{INPUT}	141.1617

Ethene

The process conditions to form maximum ethene are tabulated below

Table XIII: The process conditions for producing maximum Ethene

Variable	Value
T	835.8418
X	0
Y	0.7750835
Z	0
NINC	1
NINCO2	0
NINH2O	5
NCH4	$0.58723668 * 10^{-2}$
NCO	0.1988723
NCO2	0.7931388
NC2H6	$0.2289840 * 10^{-3}$
NC2H4	$0.8116182 * 10^{-3}$
NC3H6	$0.2589619 * 10^{-5}$
NC3H8	$0.9187669 * 10^{-5}$
NH2O	3.214850
NH2	1.771057
H_{OUT}	-983.02991
H_{IN}	-1429.150
E_{INPUT}	446.1201

Propane

Table XIV: The process conditions for producing maximum Propane

Variable	Value
T	896.8116
X	0
Y	0.9021566
Z	0
NINC	1
NINCO2	0
NINH2O	0.9021566
NCH4	0.2774660
NCO	0.2626444
NCO2	0.2645162
NC2H6	0.002681794
NC2H4	0.1232008
NC3H6	$0.3971280 * 10^{-1}$
NC3H8	$00.8639 * 10^{-2}$
NH2O	0.1104798
NH2	0.2556339
H_{OUT}	-134.3901
H_{IN}	-257.8634
E_{INPUT}	123.4734

Propene

The process conditions to form maximum propene are tabulated below

Table XV: The process conditions for producing maximum Propene

Variable	Value
T	914.0579
X	0
Y	1.107026
Z	0
NINC	1
NINCO2	0
NINH2O	1.107026
NCH4	$0.3079245 * 10^{-1}$
NCO	0.3052146
NCO2	0.2993268
NC2H6	$0.2960754 * 10^{-1}$
NC2H4	0.1018332
NC3H6	$0.2629258 * 10^{-1}$
NC3H8	$0.7635581 * 10^{-2}$
NH2O	0.2031581
NH2	0.4403743
H_{OUT}	-175.2597
H_{IN}	-316.4214
E_{INPUT}	141.1617

Mathematical Program to consider coal composition

The coal composition is used to construct a mathematical program to directly evaluate the outlet composition using the same equilibrium model as above. The general chemical reaction scheme is as follows

$$C_aH_bO_c + (\tfrac{d+e}{2})H_2O + CO_2 \longrightarrow fCO + gH_2 + hH_2O + iCO_2 + jC_nH_m$$

The appropriate constraints and optimizing variables are similar to the ones described in the previous case. The atomic balances are added per the general chemical structure shown here.

Conclusions

Some of the general trends observed in the formulation that are supported by the literature and experimental insights are

- Higher temperature favors lower carbon chain hydrocarbons and vice versa
- Higher steam inlet favor higher hydrogen and alkane concentration
- Higher Carbon Dioxide inlet concentration increases the carbon monoxide concentration and the energy usage
- Hydrogen production is both water and energy intensive

While the work could not examine the effect of coal composition due to convergence issues the general trends still would still hold good.

This work can be used to build up a much detailed mathematical program to include the effects of sulfur, ash production issues and more rigorous methods to estimate the hydrocarbon concentration.

The work also attempted to optimize the syngas composition for cases of CO:H_2 of $1:2$ and $1:4$ and future studies may concentrate on recycle and mixing streams to appropriately mix it for Fisher-Tropsch synthesis or other feedstock preparation as noted earlier in the work. The production economics of the work and further optimization of the feed stock and life cycle analysis of sulfur would be the logical progression to this work.

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