Kinetic Modelling for Coal Liquefaction Process

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Abstract- **In 1913 Bergius developed the coal hydro liquefaction. In 1917 there were clear indication of decline in domestic oil production and possibility of international shortage was realized. Around to be 1970 the chevron started coal liquefaction process. He had designed and executed the production of synthetic fuel, but had not given any kinetic model for monitoring the reaction. Our main focus is on to development a kinetic model of reaction taking place and estimating the kinetic parameter like rate constant, order of the reaction using optimization technique like regression, PSO (Particle Swamp Optimization) validating it with experimental values. The validating incorporate kinetic rate constant, conversion to cross verify the result obtained through optimization.**

Scope of this work is to get a better insight of coal liquefaction process to operate it under optimal condition. In addition to this it can gives us the various rate determining steps, so as it can be applied to variety of the coals available in the world.

Keywords- Liquefaction, Direct liquefaction, indirect liquefaction, Kinetic behavior, PSO.

I. INTRODUCTION

Coal liquefaction is a term which is used to describe a process in which a portion of the organic coal substance is converted to liquid products. In general, this includes liquids extracted by solvents. Solvent extraction has also been used extensively in research on coal structure. More specifically, coal liquefaction involves producing liquids by chemically altering the coal structure and increasing the content of hydrogen relative to carbon. At the same time, nitrogen, sulfur, oxygen, and mineral matter are removed. Compared with other fuels, coal is particularly low in hydrogen. The hydrogen consumed in producing liquids of increased hydrogen content and in removing heteroatoms represents a large part of the cost of coal liquefaction. Liquefaction methods can be classified as indirect liquefaction and direct liquefaction.

In indirect liquefaction, coal reacts with oxygen and steam at high temperature to produce a mixture of carbon monoxide and hydrogen (synthesis gas), which can be catalytically converted to liquid products. The best-known process, the Fischer–Tropsch synthesis, produces a mixture of gaseous, liquid, and solid hydrocarbons.

In direct liquefaction, coal reacts at elevated temperature and pressure with gaseous hydrogen and a solvent that is a hydrogen-donor. Conversion to liquids can be realized with or without added catalysts. According to the conditions chosen, the principal products can be high molecular mass fuels, distillate fuel Oils, gasoline, or chemical feedstocks.

The products of both indirect and direct liquefaction have higher energy content than coal. Coal typically contains 60 wt% of the heating value of the liquefied products. The liquids produced by the two methods are very different in chemical composition. Synthesis gas conversion processes give saturated hydrocarbon liquids, whereas the products of direct liquefaction are highly aromatic. These chemical differences affect the end use. Indirect liquefaction provides high-quality diesel fuel and intermediates for olefin production; direct liquefaction yields high-octane gasoline and excellent feedstocks for aromatic chemicals.

Direct and indirect liquefaction have both been used commercially to produce liquids from used commercially to produce liquids from coal. The first developments took place in Germany during the 19th century. Berthelot discovered that coal can be converted to oil by chemical reduction. Bergius (1911) demonstrated the noncatalytic conversion of coal to heavy crude oil by using a solvent and hydrogen pressure. Chevron Research Co. began research that led to development of a two-stage process, first publicly reported in 1982; thermal liquefaction in the first stage was followed by catalytic hydroprocessing in the second; direct feed of effluent from the first to the second reactor was claimed to minimize condensation of thermal products; it was scaled to 6 tons/day[1].

Above mention author have carried out the practical execution the coal liquefaction and they have shown effort of various variables on conversion yield and quality of liquid hydrocarbons obtained. Berthelot has design a two stage process to increase the yield of liquid products and shown the effect of composition on hydrogen consumption and product specification.

Above mentioned authors have not shown the kinetic study order of the reaction, kinetic rate constant determination. So we carried out this work to carryout kinetic studies and for the rate parameter estimation. Here we are using particle swarm optimization (PSO).

II. LITERATURE SURVEY

BERGIUS PROCESS:

The coal is finely ground and dried in a stream of hot gas. The dry product is mixed with heavy oil recycled from the process. Catalyst is typically added to the mixture. A number of catalysts have been developed over the years, including

tungsten or molybdenum sulfides, tin or nickel oleate, and others. Alternatively, iron sulphides present in the coal may have sufficient catalytic activity for the process, which was the original Bergius process. There are also considerations with respect to global warming, especially if coal liquefaction is conducted without carbon capture and storage technologies. The mixture is pumped into a reactor. The reaction occurs at between 400 to 500 °C and 20 to 70 MPa hydrogen pressure. The reaction produces heavy oils, middle oils, gasoline, and gases. The overall reaction can be summarized as follows:

$$nC + (n - x + 1)H_2 \rightarrow C_nH_{2n-2x+2} \qquad (1)$$
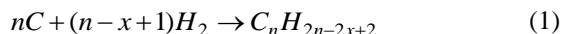
(where x = Degrees of Unsaturation)

The immediate product from the reactor must be stabilized by passing it over a conventional hydrotreating catalyst. The product stream is high in naphthenes and aromatics, low in paraffin's and very low in olefins. The different fractions can be passed to further processing (cracking, reforming) to output synthetic fuel of desirable quality. If passed through a process such as Plat forming, most of the naphthenes are converted to aromatics and the recovered hydrogen recycled to the process. The liquid product from Plat forming will contain over 75% aromatics and has a Research Octane Number of over 105.

Overall, about 97% of input carbon fed directly to the process can be converted into synthetic fuel. However, any carbon used in generating hydrogen will be lost as carbon dioxide, so reducing the overall carbon efficiency of the process.

There is a residue of unreactive tarry compounds mixed with ash from the coal and catalyst. To minimize the loss of carbon in the residue stream, it is necessary to have a low-ash feed. Typically the coal should be <10% ash by weight. The hydrogen required for the process can be also produced from coal or the residue by steam reforming. A typical hydrogen demand is ~8 kg hydrogen per ton of dry, ash-free coal. Generally, this process is similar to hydrogenation. The output is at three levels: heavy oil, middle oil, gasoline. The middle oil is hydrogenated in order to get more gasoline and the heavy oil is mixed with the coal again and the process restarts. In this way, heavy oil and middle oil fractions are also reused in this process.

THE CHEVRON COAL LIQUEFACTION PROCESS:

Chevron Research initiated a number of new studies on synthetic fuels with emphasis on 'second generation' process options. The Middle East oil embargo of 1973- 1974 was a powerful stimulant for this work, as were subsequent events in Iran and Iraq. Although the current world oil situation is less volatile, and some concerns have eased, it is nonetheless still true that sudden changes may occur with little warning. For these reasons, and because of continuing forecast declines in domestic oil production, Chevron has continued to develop synthetic fuels [1].

Chevron process description:
As this study of the liquefaction behavior of coal proceeded, it was evident that at least two separate reactions were involved. One reaction was the dissolution of the coal which seemed to require temperatures of 425°C at commercially reasonable

pressures. A second reaction was a hydrogenation /hydrocracking reaction needed to generate recycle oil and product oil. This second reaction appeared to be the most suitable for catalytic control. However, as the conditions necessary for the dissolution reaction are not necessarily optimal for recycle oil generation, the concept was developed of separating, but closely coupling, the dissolution step and the hydrogenation /hydrocracking step. This original concept has evolved into the current generation of CCLP, shown in figure below [1].

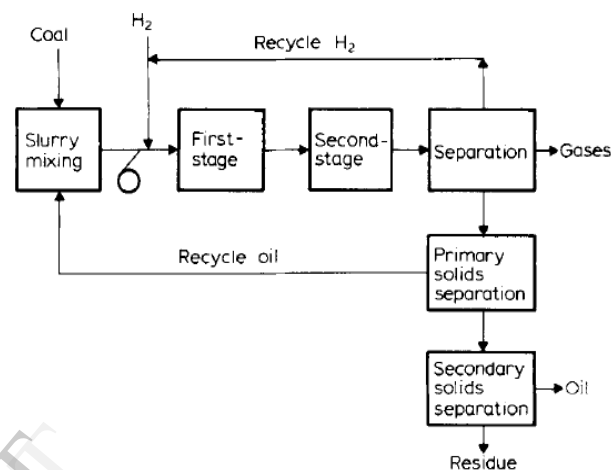Chevron two stage concept for coal liquefaction:

Fig 1 - Block diagram of chevron two stage process [1]

CCLP uses a two-stage approach to liquefaction by using two separate, but close-coupled, reaction zones. Slurry prepared from process-derived recycle oil is fed to the first-stage reactor, and effluent from this first reactor can be fed directly to the second-stage reactor containing a coal hydroprocessing catalyst. The function of the first stage is to solubilize the coal, whereas the function of the second is to stabilize the first-stage effluent and upgrade it to acceptable product and recycle oils [1].

Product distribution for coal liquefied using CCLP:

Feed coal Product (wt %)	Sub-bituminous coal	Australian brown coal
C_1-C_3	10.7	10.2
>C_4 liquid	65.2	66.1
Undissolved coal	11.8	4.5
H_2O,CO_x,H_2S,NH_3	20.0	28.0
Oil yield	4.2	4.4
H_2 consumption	195.0	218.0

Table 1- Analysis of product for CCLP[1]

III. COAL LIQUEFACTION PROCESS IS TWO TYPES

1. Direct coal liquefaction (DCL)
2. Indirect coal liquefaction,(ICL)
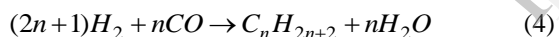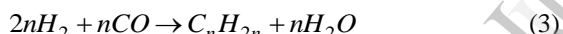
1. DIRECT COAL LIQUEFACTION PROCESS:

Direct liquefaction of coal is conventionally referred to such a chemically thermal decomposition process in which coal, as raw material, at high temperature, under high hydrogen pressure, and in the presence of catalysts, is finally converted to liquid hydrocarbon mixtures as well as lesser amount of gaseous hydrocarbons meanwhile heteroatoms, e.g. nitrogen, oxygen, sulfur, etc., are chemically removed. Direct liquefaction process mainly consists of the following steps: crushing and drying of coal; preparation of coal slurry; hydro liquefaction; separation of liquid products from solid residues; purification and refine of liquid products [2,3].

2. INDIRECT COAL LIQUEFACTION:

Indirect liquefaction of coal is a stepwise process. The coal first reacts with steam and oxygen (gasification) to produce a raw mixture of carbon monoxide and hydrogen known as synthesis gas or syngas. The water–gas shift reactor adjusts the ratio of hydrogen to carbon monoxide to the requirements of a particular synthesis by means of a reversible reaction between steam and carbon monoxide.

$$H_2O_{(g)} + CO \leftrightarrow H_2 + CO_2 \qquad (2)$$

After purification, the clean syngas is catalytically converted to a wide range of products, such as hydrocarbons, alcohols, aldehydes, ketones, and acids. Production of predominantly liquid hydrocarbons from syngas is known as the Fischer–Tropsch synthesis, which is a commercial process for converting coal into substitute natural gas, gasoline, diesel oil, wax, and alcohols. Production of hydrocarbons and alcohols by the Fischer–Tropsch synthesis can be represented as follows.

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \qquad (3)$$

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \qquad (4)$$

$$2nH_2 + nCO \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad (5)$$

Where n is an integer.

Reaction (3) represents formation of olefins, reaction (4) of alkanes, and reaction (5) of alcohols. Hydrocarbon products are in the gasoline boiling range (50-180^{0}C), but not directly suitable for gasoline use because straight-chain structures predominate, giving an intermediate octane number as low as 55-65. The intermediate octane number is defined as the average of the research and motor octane numbers. Extensive further treatment is needed to meet octane requirements for gasoline. However, the fraction that boils between 180 and 320^{0}C has a high cetane number (65-75) and provides valuable diesel fuel with little or no additional refining.

The primary step in the development of indirect liquefaction is the production of clean synthesis gas; thus, development of coal gasification parallels the success of indirect liquefaction [2,3].

IV. COAL LIQUEFACTION PROCESS WITHOUT CATALYST:
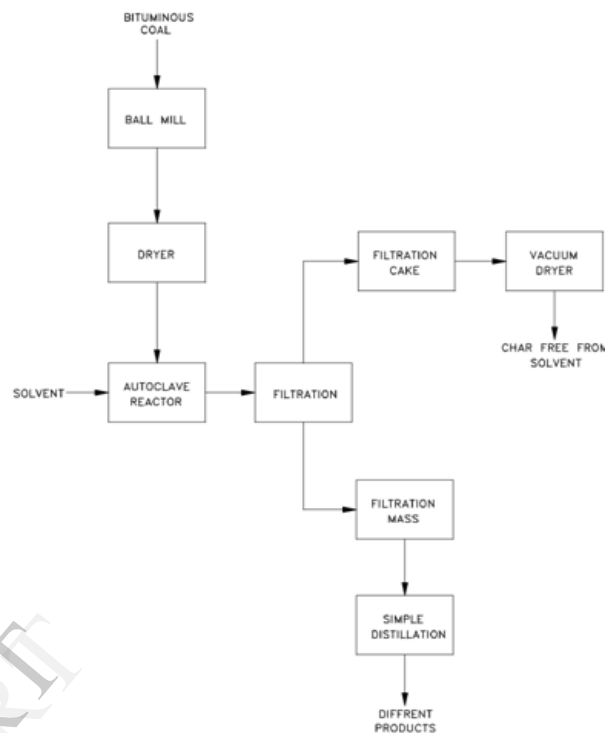
Block diagram of direct coal liquefaction process:

Fig 2 -Block diagram of direct coal liquefaction process without catalyst

Proximate Analysis of Initial Bituminous Coal:

Content	Weight %
Moisture Content	8.12%
Volatile Material	44.07%
Ash	10.88%
Fixed Carbon	37.30%

Table 2 - Proximate analysis initial sample

Proximate Analysis (Bituminous Coal drying 5hr under nitrogen atmosphere):

Content	Weight %
Moisture Content	3.39%
Volatile Material	48.50%
Ash	11.44%
Fixed Carbon	37.12%

Table 3-Proximate analysis of drying sample

Process description:

First the size is reduced of the bituminous coal by using ball mill. After that dry the coal at 110^oC and nitrogen atmosphere up to 5hrs by using dryer. Take dry bituminous coal sample mixed with solvent with ratio 1:4. Give heating up to 320^0C and 70 kg/cm^2 and maintain 2 hr. at this condition. Then stop heating and cool the autoclave up to atmospheric temperature. Then remove reaction mass from the autoclave. All reaction mass is filtered by using vacuum filtration. Collect all the filtrate at bottom and cake from top. The filtrate reaction mass separated by using simple distillation according to the boiling point of the components. The component is detected by using gas liquid chromatography. According to the boiling point the expected products are (benzene, toluene, xylene, α,β-naphthol, phenol, cresol). Dry the cake at 110^oC under vacuum for 2 hrs for removal of solvent.

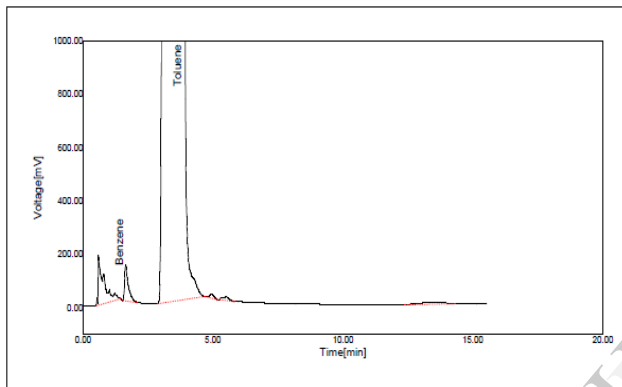## RESULTS FROM GAS LIQUID CHROMATOGRAPHY
Fraction-1

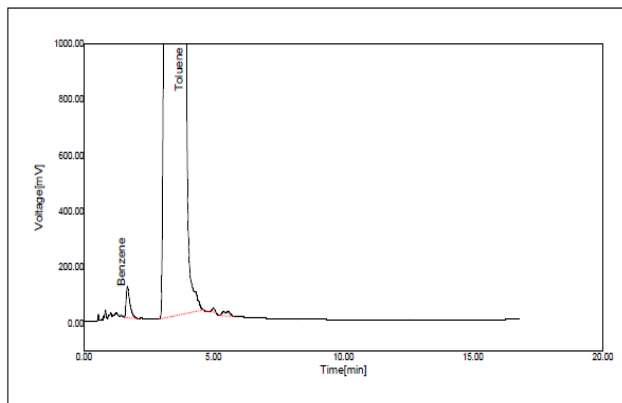Fig 3 -Gas chromatography result for fraction 1

Fraction-2

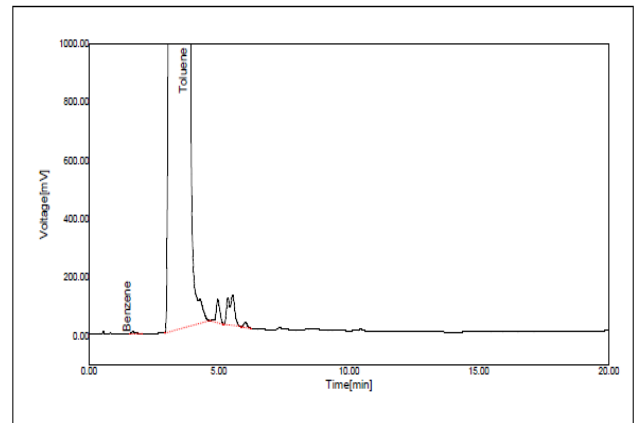Fig 4 -Gas chromatography result for fraction 3

Fraction-3

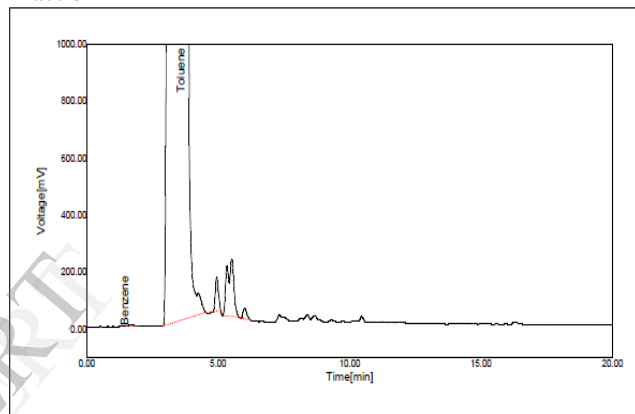Fig 5 -Gas chromatography result for fraction 3

Fraction-4

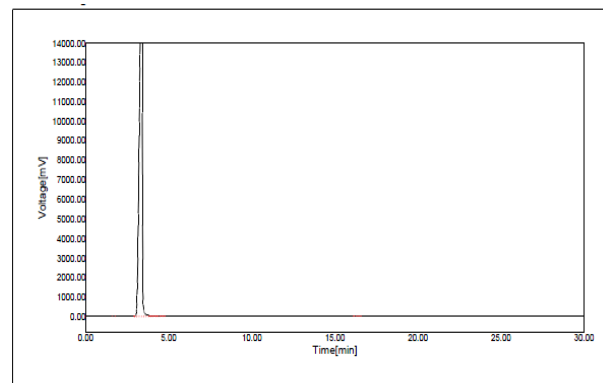Fig 6 -Gas chromatography result for fraction 4

Residue

Fig 7 -Gas chromatography result for fraction 5

V. REGRESSION METHODS

There are two types of regression method

1. Linear regression
2. Nonlinear regression

Nonlinear regression: PSO

Particle swarm optimization (PSO)

1. Particle Swarm optimization is an heuristic optimization method and the algorithm is based on the simulation of collective behavior of animals.

2. The PSO algorithm starts with the randomly generated initially generated particles, and each particle in the parameter space is associated with a definite velocity.

3. During such process, particles fly through the parameter space with velocity which are dynamically adjusted according to their historical behavior, and particles have tendency to fly towards the global minimum.

4. PSO followed by Levenberg Marquardt algorithm [5].

Hybrid minimization algorithm:-

1. Normally, heuristic optimization methods such as generic algorithm (GA), simulation annealing (SA) and particle swarm optimization (PSO) are based on empirical evolutionary rules that frequently mimic successful optimization strategies found in nature.

2. The heuristic optimization method such does not determine the exact optimum solution because of the randomness and its gives a good approximately of the searched optimum solution.

3. Therefore, a combination of heuristic and gradient based optimization methods for parameter estimation is very promising.

4. Here, the former method does the global search in the parameter space and determines the required global minimum.

5. The latter algorithm takes the global minimum determined from the heuristic method as initial guesses and does the necessary local search around the global minimum and determines the required optimal parameters.

6. The PSO algorithm is given by:

$$v_{p,d,j}^{i+1} = w_{\text{int}} v_{p,d,j}^i + c_1 r_1 \left(x_{p,j}^{ind} - x_{p,d,j}^i \right) + c_2 r_2 \left(x_j^{glo} - x_{p,d,j}^i \right) \quad (6)$$

$$x_{p,d,j}^{i+1} = x_{p,d,j}^i + v_{p,d,j}^{i+1} \quad (7)$$

7. The PSO parameters such as w_{int}, c_1 and c_2 represent the inertial weight, the cognition and social parameters respectively.

8. The two equations describe the update of particle velocity and the position respectively.

9. The first equation consist of three parts namely, the momentum, cognitive and social parts .

10. The cognitive and social parts represent the private thinking itself and the collaboration among particles respectively.

11. In the present PSO algorithm, a separate index is created for number of parameter to be estimated with Np dimension. Thus, the algorithm allows us to conduct both the uni-directional as well as multi directional search in the parameter space [5].
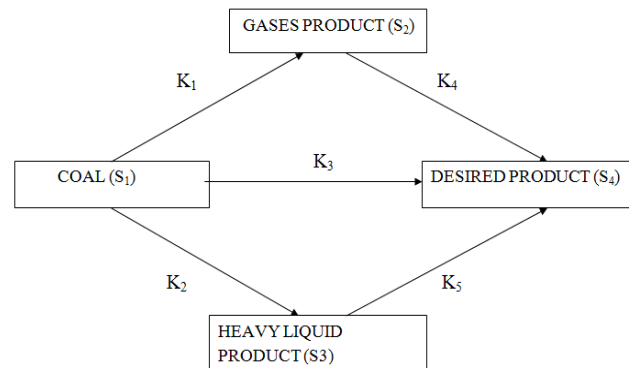
Stoichiometry for coal to desired product:

Fig no 8-Schematic representation of coal reaction [4]

MODEL EQUATION:

A general mole balance equation over an isothermal ideal batch reactor is governed by the ordinary differential equations, and it represents the time dependence of the mole fraction of species i.

$$\frac{dz_{s_i}}{dt} = \sum_{j=1}^{i-1} k_{i,j} z_{s_j} - \sum_{j=i+1}^{N_s} k_{j,i} z_{s_i} \quad (8)$$

Here, i varies from 1 to N_s. The reaction rates are written from law of mass action kinetics, and are given in eq. (8). Here, the first term on the right hand side of the mole balance equation represents the formation of species i from the reactant j, and the second term indicates that the disappearance of the reactant i into different products in all possible ways. In eq. (8), the sum of mole fractions of all the species is equal to the sum of the initial mole fraction of the species in the feed at all time instances [5].

VI. RESULTS

Estimated kinetic parameters for the four species reacting system. Estimated kinetic parameters: k = [0.51 0.3 0.2 0.7 0.1]

Component	Mathematical (mol %)	Experimental (mol %)	Difference (mol %)
Benzene	0.515	0.533	0.0180
Toluene	99.21	99.313	0.0130
Xylene	0.274	0.155	0.1190

Table 4 -Result of theoretical and practical data

SIMULATED RESULT:

Kinetic constant matrix
k = [0 0 0 0; 0.4200 0 0 0; 0.1621 0.0016 0 0; 0.6480 0.5922 0.5922 0]

Time	S_1	S_2	S_3	S_4
0	1.0000	0	0	0
0.1	0.8843	0.0383	0.0148	0.0626
0.2	0.7819	0.0700	0.0270	0.1210
0.3	0.6914	0.0960	0.0371	0.1755
0.4	0.6114	0.1170	0.0452	0.2265
0.5	0.5406	0.1337	0.0517	0.2741
0.6	0.4780	0.1467	0.0567	0.3185
0.7	0.4227	0.1566	0.0606	0.3602
0.8	0.3738	0.1637	0.0634	0.3991
0.9	0.3305	0.1686	0.0653	0.4356
1.0	0.2923	0.1716	0.0664	0.4697
1.1	0.2584	0.1729	0.0670	0.5017
1.2	0.2285	0.1728	0.0670	0.5317
1.3	0.2021	0.1716	0.0665	0.5598
1.4	0.1787	0.1695	0.0657	0.5861
1.5	0.1580	0.1666	0.0646	0.6108
1.6	0.1397	0.1630	0.0633	0.6340
1.7	0.1235	0.1590	0.0617	0.6557
1.8	0.1092	0.1546	0.0600	0.6762
1.9	0.0966	0.1498	0.0580	0.6953
2.0	0.0854	0.00437	0.0030	0.9926

Table 5-Output of simulated result

D-coefficient matrix
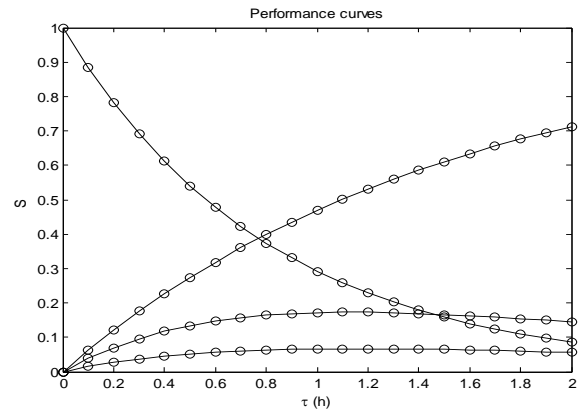
D= [1.0000 0 00;-0.6601 0.6601 0 0; -0.2525 -0.6601 0.9125 0;-0.0875 -0.0000 -0.9125 1.0000]

Fig no 9- Performance curve

VII. CONCLUSION

1. Coal liquefaction is an alternative coal conversion process to light oils and other value added chemicals.
2. From the preliminary investigation it is found that conversion of volatiles from the coal to BTX started at above 318^0C and 70 bar pressure. Nearly 17% conversion on basis coal and 35 % conversion on basis volatiles are achieved.
3. There are six components observed in GC analysis and out which benzene, toluene and xylene are qualitatively identified with available analytical facilities.
4. The detail investigation may be carried out with more variation of operating parameters with use of catalyst and equipped analytical facilities to optimize the product yield and detail product quantification.
5. The Kinetic model proposed has been simulated using MATLAB and compared with experimental results.
6. The proposed kinetic model formed to be in agreement with the experimental results with a slight deviation and this multi objective function can be be simulated using higher breed of optimizing algorithm like HPSO to obtained more profound results.

VIII. NOMENCLATURE

- *p* denotes the particle
- *d* is the search direction
- *j* denotes the parameter index
- *i* represent the iteration number
- *v* is the velocity of the particle
- *x* is the position of particle
- x^{ind} is the best position found by the particle itself
- x^{glo} is the best position found by the whole swarm
- r_1 & r_2 are two random numbers with uniform distribution in the range (0,1)
- τ represents residence time

- *Dm is* the axial dispersion coefficient
- *L* is the length of the reactor
- σ^2 is the variance
- *N* is the equivalent number of completely stirred tanks in series.
- *i* is the formation of species
- *j* is the reactant

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