A Two-Step, Temperature-Staged Direct Coal Liquefaction Process

Reyna Singh, David Lokhat, Milan Carsky

Abstract—The world crude oil demand is projected to rise to 108.5 million bbl/d by the year 2035. With reserves estimated at 869 billion tonnes worldwide, coal remains an abundant resource. The aim of this work was to produce a high value hydrocarbon liquid product using a Direct Coal Liquefaction (DCL) process at, relatively mild operating conditions. Via hydrogenation, the temperature-staged approach was investigated in a dual reactor lab-scale pilot plant facility. The objectives included maximising thermal dissolution of the coal in the presence of tetralin as the hydrogen donor solvent in the first stage with 2:1 and 3:1 solvent: coal ratios. Subsequently, in the second stage, hydrogen saturation, in particular, hydrodesulphurization (HDS) performance was assessed. Two commercial hydrotreating catalysts were investigated viz. Nickel-Molybdenum (Ni-Mo) and Cobalt-Molybdenum (Co-Mo). GC-MS results identified 77 compounds and various functional groups present in the first and second stage liquid product. In the first stage 3:1 ratios and liquid product yields catalysed by magnetite were favoured. The second stage product distribution showed an increase in the BTX (Benzene, Toluene, Xylene) quality of the liquid product, branched chain alkanes and a reduction in the sulphur concentration. As an HDS performer and selectivity to the production of long and branched chain alkanes, Ni-Mo had an improved performance over Co-Mo. Co-Mo is selective to a higher concentration of cyclohexane. For 16 days on stream each, Ni-Mo had a higher activity than Co-Mo. The potential to cover the demand for low–sulphur, crude diesel and solvents from the production of high value hydrocarbon liquid in the said process, is thus demonstrated.

Keywords—Catalyst, coal, liquefaction, temperature-staged.

I. Introduction

A. Historical Overview

BEING a descendant of the Bergius process, the DCL process is burdened with a number of disadvantages including severe operating conditions and the use of an iron-based catalyst of poor activity. Further development of the DCL process was based on this 1920s technology, with the major objectives being relaxing of operating conditions, increasing the liquid yield and lowering the hydrogen consumption.

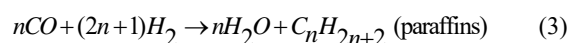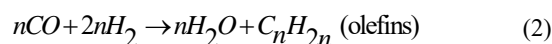The two-stage DCL process has been supported by the United States Department of Energy in the past as an overall process for the production of high value liquid hydrocarbons in which the first stage involves initial dissolution at mild conditions, followed by the more severe catalytic hydrogenation-hydrocracking step [1].

B. Chemistry of the Coal-to-Liquid (CTL) Process [2]

Carbon monoxide can be produced by gasification or using another carbon rich compound. The necessary reaction energy is supplied by steam or oxygen.

$$C + \frac{1}{2}O_2 \rightarrow CO \tag{1}$$
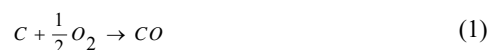
The resulting mixture of carbon monoxide and hydrogen is called synthesis gas (syngas). In the presence of a suitable catalyst, syngas is used to construct hydrocarbon chains of different lengths. Generally, the Fischer Tropsch (FT) process yields two product types, olefins and paraffins.

$$nCO + 2nH_2 \rightarrow nH_2O + C_nH_{2n} \text{ (olefins)} \tag{2}$$

$$nCO + (2n+1)H_2 \rightarrow nH_2O + C_nH_{2n+2} \text{ (paraffins)} \tag{3}$$

The selectivity to olefins or paraffins depends on the catalysts used and the reactor operating conditions. Olefin-rich products with 'n' in the range of 12-19 are suitable for making synthetic diesel and solvents in the low temperature FT-process.

In the DCL process, the coal is split into shorter hydrocarbons; resembling ordinary crude oil. This process occurs by adding H_2 under high pressure and temperature, thus eliminating the need for a gaseous middle stage.

$$nC + (n+1)H_2 \rightarrow C_nH_{2n+2} \tag{4}$$
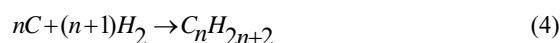
Coal is a chemically complex substance consisting of aromatic polymers. In order to obtain liquid fuel, the necessity for a two-stage process involving an initial thermal dissolution step followed by hydrotreating can is described by Fig. 1. In the DCL process the typical reaction mechanism is such that three main products i.e. solid residue consisting of char and coke, liquid and gas are formed [4].

$$Coal + H_2 + Solvent \rightarrow Solid\ Residue + Liquid + Gas \tag{5}$$

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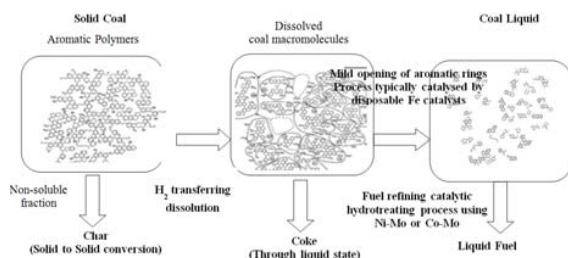
Fig. 1 Formation of liquid fuel from a two-step process [3]

C. Tetralin as the Hydrogen Donor Solvent

In studying the role that tetralin plays as the hydrogen donor solvent, it is understood that as coal dissolves, hydrogen must be consumed. Free radicals are formed from the thermal disruption of weak bonds in the coal structure. For solubility to be achieved these radicals must be capped by hydrogen or they will recombine.

The supply of hydrogen can come from a number of sources, such as from the coal, gaseous hydrogen or from a hydrogen donor solvent. In order to maximise on thermal dissolution or to maximise on the hydrogen-donor solvent refining process, the most efficient and dominant source is considered to be hydro-aromatics in the donor solvent.

The tetralin and naphthalene interconversion and hydrogen transfer can be described by the reversible reaction below [6].

$$\text{Naphthalene} + 2H_2 \underset{}{\overset{K}{\rightleftarrows}} \text{Tetralin} \qquad (6)$$
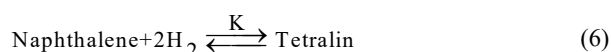
When coal is treated with tetralin in the absence of catalyst for 1 hour at 455 °C, the presence of hydrogen atmosphere is important to increase the conversion and also to increase the amount of sulphur removed. When hydrogen pressure is used instead of nitrogen, the sulphur removal rate is doubled in the product oil [7].

D. Catalysts

First stage iron-based, dispersed catalyst: Magnetite (Fe_3O_4) is documented as one of the major shortfalls associated with the CTL technology is the use of expensive catalysts which are not easily recovered from the process [2].

Advantages of using magnetite:
- Easily recoverable from waste coal which is unconverted
- Abundant, inexpensive disposable catalyst
- Known to enhance yields
- Presents no environmental hazard
- Proven to catalyse hydrogenation reactions

Second stage hydrotreating catalysts:

Hydrotreating catalysts Co-Mo and Ni-Mo typically function to achieve HDS and hydrodenitrogenation (HDN) performance [5]. HDS is a process where a hydrogen donor reacts with coal; and a substantial amount of sulphur, oxygen, and nitrogen in the coal is eliminated as hydrogen sulphide, water and ammonia. This elimination could be a direct result of the cleavage of the hetero-bonds presents in the coal.

In this study, the focus was on HDS typically described by the reaction (7).

$$[R\text{-}S] + H_2 \xrightarrow[300\text{-}450°C]{\text{Catalyst}} [R\text{-}H] + H_2S \qquad (7)$$
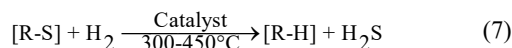
[R-S] can be described as the sulphur containing hydrocarbon compound and [R-H] as the resultant aliphatic hydrocarbon product. The variables which influence this reaction are the nature and the amount of the hydrogen-donor solvent, the presence and absence of hydrogen pressure, the level of this pressure, the reaction temperature, the reaction time, and the nature (rank and type) of the coal.

II. MATERIALS AND METHODS

A. First and Second Stage Experiments

High grade bituminous coal samples used in this study were obtained from the Exxaro Grootegeluk Mine GG1 Coal Preparation Washing Plant. Petrographic and chemical analysis of the samples was conducted by the Bureau VERITAS Inspectorate Laboratory for Advanced Coal Technology (HJ Roux, 2012); and pulverised to 90-100μm. tetralin (Sigma Aldrich, 99%) was used as the hydrogen donor solvent. This coal was dried under vacuum at 100°C for 2 hours to obtain samples on a moisture free basis [8]. The feed slurry consisted of 100g of coal and tetralin mixed in 2:1 and 3:1 solvent/coal ratios. The first stage magnetite catalyst was prepared in-situ and added to the feed slurry at 0.25wt% of the dry coal feed. The first stage thermal dissolution process took place in a 1 litre, T316 stainless steel agitated batch reactor with a mechanically driven stirrer (Parr Series 4521 Bench Top Reactor). The product from the first stage was filtered under vacuum. In the second stage of the process; there were constraints on the pumping capacity and volume of the fixed bed reactor. Due to these constraints, the filtered liquid products from the first stage runs were divided into 15ml aliquots and processed in the corresponding second stage runs. The liquid was charged into a pressurized stainless steel reservoir before being pumped into the fixed bed reactor. The second stage fixed bed reactor was made of a ¾ inch OD 316 SS tube. The catalyst bed comprised the hydrotreating catalysts and 4mm glass beads to maintain the bed length and to aid in gas-liquid distribution. Cobalt Molybdenum (HDMax 200, Clariant) (C49-1-01) 3mm extrudate and Nickel Molybdenum (HDMax 300 TRX, Clariant) (C20-7); 1.3mm extrudate were used. The Co/Mo/Al$_2$O$_3$ was Clariant Type containing approximately 15 wt. % MoO$_3$ and 3wt. % CoO on silica-stabilized alumina (5% SiO2). The Ni/Mo/Al$_2$O$_3$ was Clariant Type containing approximately 15 wt. % MoO$_3$ and 3wt. % Ni on silica-stabilized alumina (5% SiO2). These catalysts were activated at 300°C with a hydrogen flowrate of approximately 10 ml/min prior to the testing. The temperature of the 33.5cm heated bed length was measured by a 1/8 inch thermocouple pocket inside the insulated furnace to measure the reactor temperature. The reactor pressure was monitored by a pressure gauge, and the rig was protected from over pressure by a relief valve set at 180barg. Hoke non-return valves were selected and all other valves and fittings were Swagelok branded and selected to withstand system operating temperature and pressure.

The reactor temperature and pressure were maintained by a furnace and downstream main product valve.

Liquid feed was supplied by a positive displacement liquid chromatograph piston pump. A gas-liquid separator located at the outlet of the reactor ensured that the gas was exhausted to the online VARIOplus gas analyser and vent; and the liquid was collected and sampled for analysis. The gas analyser was operated to record per second gas quality and calibrated to detect and quantify CO and CH_4 for heavy gas fuel.
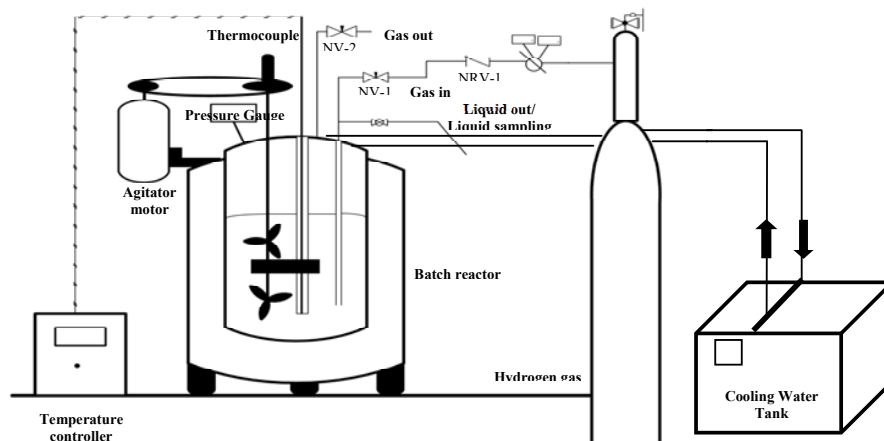

Fig. 2 First stage batch reactor (drawing not to scale)

TABLE I
CHEMICAL ANALYSIS OF THE COAL SAMPLES TAKEN FROM THE EXXARO GROOTEGELUK GG1 COAL PLANT USED IN THIS STUDY [11]

Property		Value
Moisture	%	2.3
Ash	%	10.4
Volatile matter	%	36.9
Total sulphur	%	1.10
Pyritic sulphur	%	0.14
Sulphatic sulphur	%	0.02
Organic sulphur	%	0.94
Carbon	%	72.86
Hydrogen	%	4.93
Nitrogen	%	1.52
Oxygen	%	9.15
Fixed carbon	%	51.4
Gross calorific value	MJ/kg	29.42

TABLE II
VALVE INVENTORY

Key	Valve description
BV-	Ball valve
PRV-	Pressure relief valve
NRV-	Non-return valve
NV-	Needle valve
TWV-	3-way valve

B. Analytical Methods

Using the method of internal standards, quantification for the various functional organic groups was accomplished. These procedures were guided by the ASTM standards set out by the Manual of Hydrocarbon Analysis [9]. All solvents used were of highest purity and reagent grade. All samples were run prior to dilution and thereafter spiking with the internal standard, in order to rule out potential interaction effects between pure samples, solvents and internal standards. The use of deuterated internal standards is considered to be standard practice for quantifying polycyclic aromatic hydrocarbon (PAH) compounds [10].

For both the light and heavy fraction analysis, the Zebron ZB-5ms column was used in the Shimadzu Gas Chromatography Mass Spectrometer instrument.

In preparing the GC-MS calibrations for the various functional groups, a large concentration range was used in order to envelop the concentrations for all test samples. In the case of ethylbenzene, a concentration range of 5-1000ppm was used to quantify for the alicyclic hydrocarbon compounds.

The GC-MS temperature profile included that, for light components; the sample would be injected in the split mode at an injection temperature of 280℃. The ion source temperature was 200℃.

Included in the 35 minute temperature profile was that the column temperature would be initially held at 30℃ for 1 minute, raised to 50℃ at the rate of 5℃/min and held for 10 minutes, then to 80℃ at the rate of 5℃/min and held at this final temperature for 10min. Detector temperature was kept at 280℃.

For heavy component analysis, the samples were injected in the split mode at an injection temperature of 280℃. The transfer line temperature was 200℃. The 44 minute temperature profile included that the column temperature was initially held at 210 ℃ for 5minutes, raised to 215℃ at the rate of 5℃/min, then to 220 ℃ at the rate of 10℃/min, and finally to 230℃ at the rate of 10℃/min and held at this final temperature for 10min.
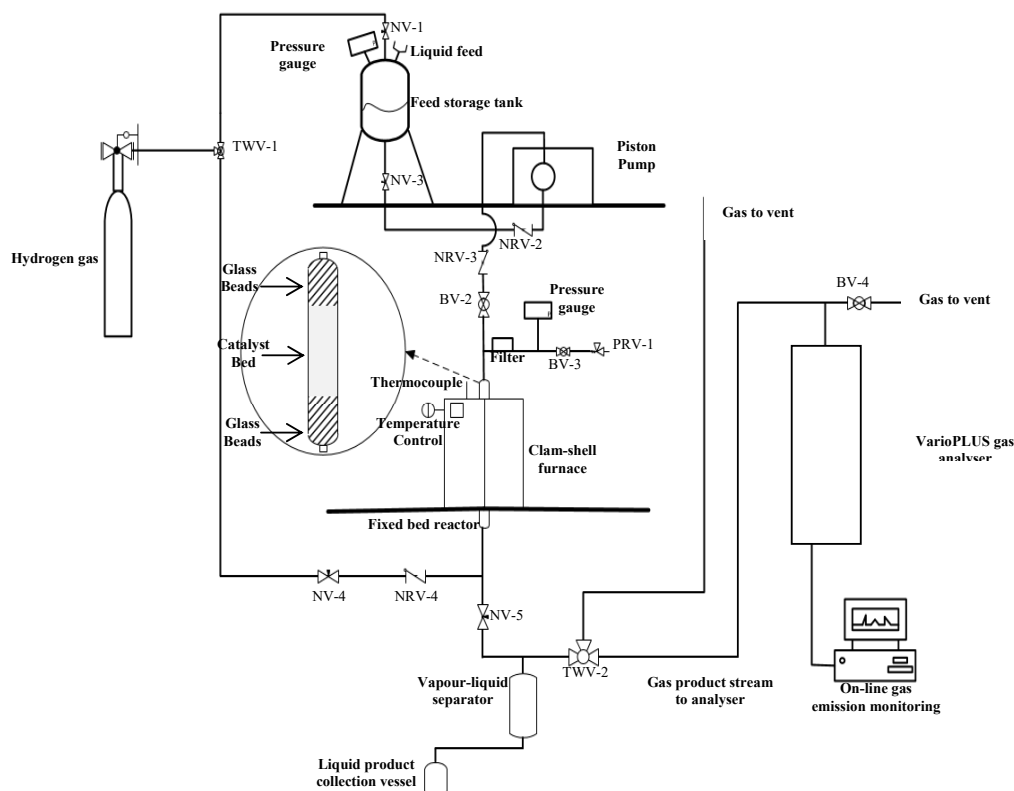
Fig. 3 Second stage hydrotreating pilot-plant facility (drawing not to scale)

For both the heavy and light component analysis, mass spectrometry was acquired using the electron ionization (EI) and selective ion monitoring (SIM) modes. There was also the strong presence of unquantified compounds including acetic acid, cyclobutanol and spirodecane.

TABLE III
SEMI-VOLATILE DEUTERATED INTERNAL STANDARD MIXTURE CONTAINING CERTIFIED REFERENCE MATERIALS [12] USED TO QUANTIFY COMPOUNDS IN COAL DERIVED LIQUID PRODUCT

Analyte	Certified Purity (%)	Analytical Concentration ($\mu g/ml$)
1,4-Dichlorobenzene-D4	99.9	1878.5
Naphthalene-D8	96.3	1919.6
Acenaphthene-D10	99.9	1930.6
Phenanthrene-D10	98.7	1846.6
Chrysene-D12	98.8	1807.7
Perylene-D12	99.7	1964.1

TABLE IV
SOLVENTS AND INTERNAL STANDARDS USED FOR QUANTIFICATION IN GC-MS ANALYSIS

Solvent	Internal Standard	Functional Organic Group
Propan-1-ol	Semi-volatile deuterated mixture,	PAH Compounds
Propan-1-ol	Ethylbenzene (Fluka, ≥98%)	Alicyclic Hydrocarbons (BTX)
Propan-1-ol	Pentene (Fluka, 99%)	Paraffins
Hexadecane	Sulfolane (Sigma Aldrich, 99%)	Sulphur

TABLE V
GC-MS ANALYTICAL CONDITIONS

Parameter	Light Fractions	Heavy Fractions
Column Oven temperature (℃)	30	210
Split ratio	200	70
Injection temperature (℃)	280	280
Carrier gas	Helium	Helium
Sample volume (μl)	0.50	0.50
Carrier gas pressure (kPa)	46.60	100.10
Carrier gas flowrate (ml/min)	1.01	0.87

C. Design of Experiments

For both the first and second stages of the process, a factorial design was applied.

For the first stage baseline and catalysed experiments, 3 factors were tested: solvent: coal ratio (X1), temperature (℃) (X2), reaction time (minutes) (X3). Each factor was tested at 2 levels as indicated in Table VI. The conversion to liquid and gas product were considered the response variables. The liquid product response variable was commented on in accordance with the product distribution results obtained in the GC-MS chromatograms.

For both the baseline and catalysed runs, which is based on the 2^3 factorial designs, a total of 16 experiments were conducted. That is 8 combinations for the baseline experiments and 8 combinations for the catalysed runs excluding replications. For the second stage Ni-Mo and Co-Mo experiments 3 factors were again tested. Using the first

stage baseline and catalysed products, each factor was tested at 2 levels using the temperature staged approach.

TABLE VI
EXPERIMENTAL DESIGN

Design factor	Upper level	Lower level
First Stage		
X1: solvent/coal ratio (dimensionless)	3:1	2:1
X2: temperature (℃)	300	250
X3: reaction time (minutes)	60	30
Second Stage		
XI: solvent/coal ratio (dimensionless)	3:1	2:1
XII: temperature (℃)	350	300
XIII: reaction time (minutes)	60	30

The experiments were designed such that 15 ml samples of the first stage product were tested in both the Co-Mo and Ni-Mo second stage systems. Thus Co-Mo and Ni-Mo were on stream for 16 days each. The response variables were again the liquid and gas yields. Moreover, in the second stage testing emphasis was placed on reporting the responses in accordance with the gas analysis results and the product distribution obtained from the GC-MS.

III. RESULTS

A. Yields

The focus of the study was on obtaining a high value liquid product leaving the second stage of the process. With reference to Fig. 4, highest liquid yields were experienced in the lower temperature range, for a 3:1 solvent/coal ratio and for a 60 minute reaction period.

With reference to Figs. 5 (a) and (b) respectively, the gas and liquid yields show no significant difference in the yields between Co-Mo and Ni-Mo. Higher liquid yields were observed at 350℃ .

B. Gas Chromatography-Mass Spectrometry

Fig. 6 is representative of the GC-MS results obtained in this study when pure product samples were analysed.

Chromatogram set (a) is a superimposed image of the first stage product distribution using the magnetite catalyst in the feed slurry; with a second stage chromatogram obtained using Ni-Mo catalyst. As compared to the first stage, evident is the change in product distribution. The second stage Ni-Mo results produced a higher conversion to the PAH compounds, alicyclic hydrocarbons. In the form of thiophenes and sulphuric acid, sulphur containing compounds were identified in the first stage; sulphur containing compounds were identified in trace amounts in the second stage results or not detected altogether. There was a strong presence of sulphur in the form of sulphuric acid in the first stage product.

$$2S + 4O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad (8)$$
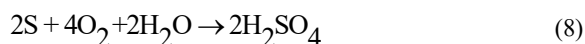
Chromatogram set (c) is a representation of the typical results obtained from the second stage pilot plant showing a full scale light and heavy product distribution. In the light

fractions, alicyclic compounds in the form of BTX compounds were mostly identified and paraffins in the C_4-C_{11} range. In the heavy fractions, PAH compounds were present as well as paraffins in the C_{12}-C_{24} range. Benzene was detected in higher concentrations with the use of Co-Mo as opposed to Ni-Mo. For Co-Mo, benzene was detectable in both the light and heavy fraction product distribution. With a high concentration of benzene and benzene 1, 2, 4-trimethyl detected in the heavy fraction GC-MS temperature profile. In the light component temperature profile benzene and 1, 2, 4-triemthyl were detected in concentrations between 50-500ppm. In the heavy component analysis, the benzene concentrations ranged between 1000 to 5000ppm. Toluene and m, o and p-xylene were concentrated in the light fractions in NiMo and CoMo. Higher concentrations of toluene and xylene were detected in the light fractions of NiMo between concentrations of 500 to 1000ppm. Cyclohexane was concentrated in the light fractions only. For Ni-Mo cyclohexane concentration ranged between 5-50 ppm whereas, for Co-Mo there was a marked increase in concentration of cyclohexane with concentrations ranging from 50-500ppm.
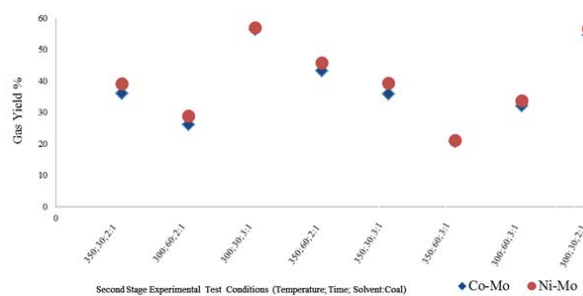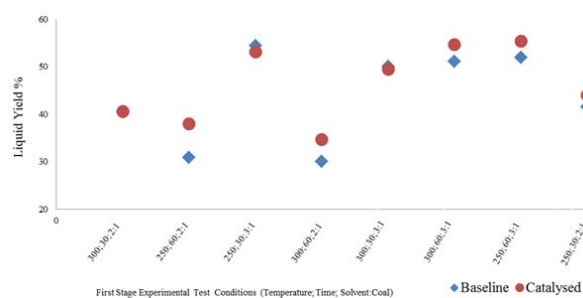

Fig. 4 First stage liquid yields

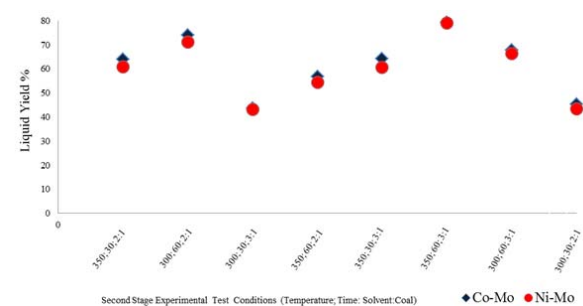Fig. 5 (a) Gas yields from Co-Mo and Ni-Mo experimental runs

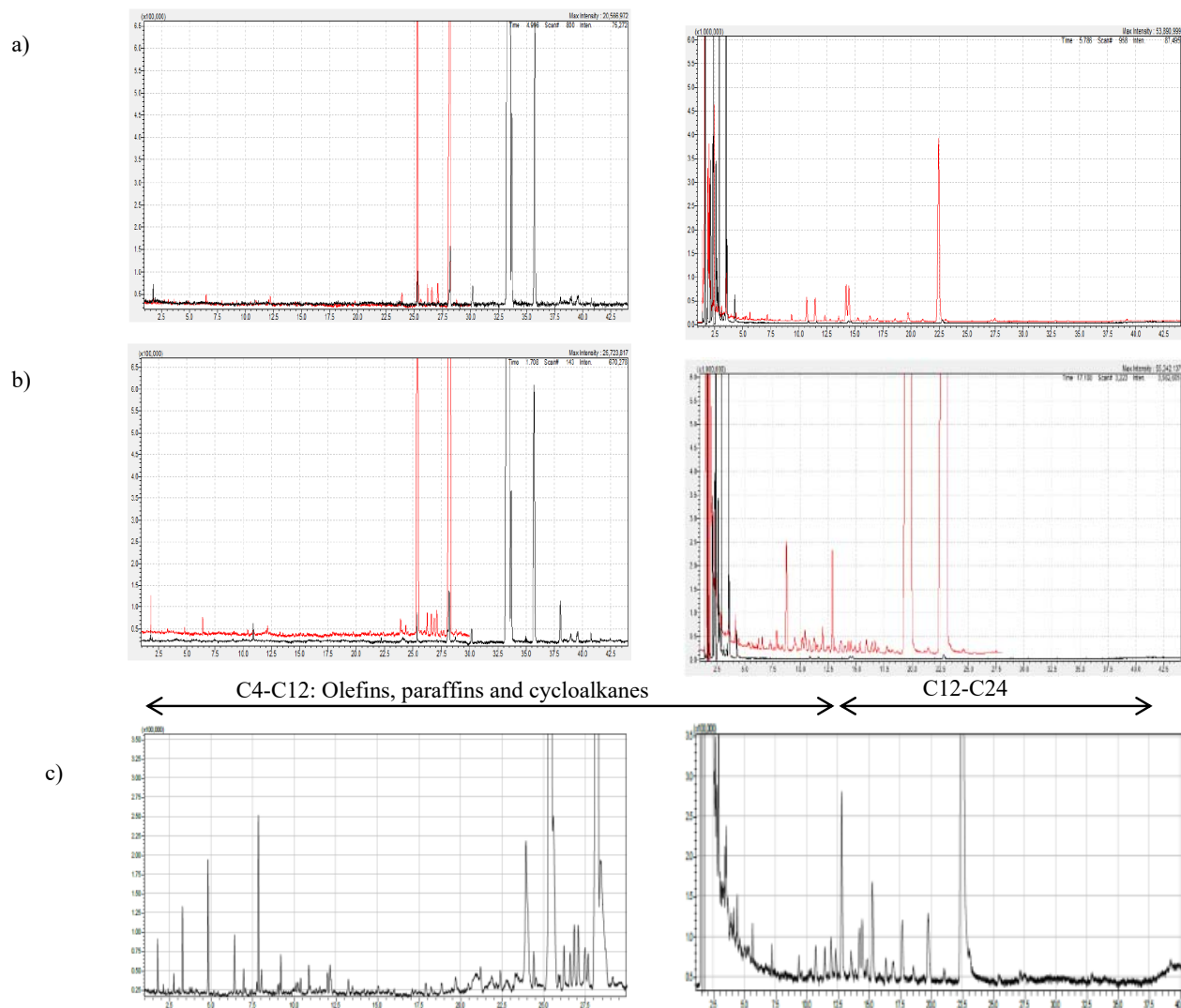Fig. 5 (b) Liquid yields from Co-Mo and Ni-Mo experimental runs

a)

b)

C4-C12: Olefins, paraffins and cycloalkanes   C12-C24

c)

Fig. 6 GC-MS chromatograms taken from first and second stage liquid product analysis
(a) First and second stage eluted fractions left (light fractions) and right (heavy fractions) of first
stage (black) superimposed with the second stage Ni-Mo results (red).
(b) First and second stage eluted fractions left (light fractions) and right (heavy fractions) of first
stage (black) superimposed with the second stage Co-Mo results (red).
(c) Light and heavy second stage eluted fractions and product distribution in the range of C_4-C_{24} for
Ni-Mo at favourable operating conditions.

The PAH compounds were concentrated in the heavy fractions, these compounds typical to coal tar and coke included phenanthrene, chrysene, anthracene, perylene and naphthalene together with its derivatives. It was observed that for the second stage temperature of 350℃, there was an increase in the concentration of these compounds by an order of magnitude. In particular, a higher concentration of naphthalene and its derivatives, which could attributed to the directly proportional temperature relationship [6]. Also concentrated in the heavy fractions was a large concentration of pentadecane, eicosane, heptadecane, tetracontane, tetracosane, branched long chain hydrocarbons including pentadecane, 8-hexyl, undecane, 5-ethyl-5-propyl. There is a large concentration of cyclohexane compounds and its derivatives (including cyclohexane, ethyl cyclohexane, methyl cyclohexane, methyl cyclopentane) present in the second stage process with Co-Mo used as the catalyst. Contrary to this result, the product obtained from the use of Ni-Mo included aliphatic hydrocarbons particularly, nonane (Shellsol140) and dodecane. Significant is that the concentration of long, branched alkanes present in the heavy fractions is greater than the short chain alkanes present in the light fractions. Short chain alkanes in the light fractions did not exceed 100ppm. Nonene was detected in small concentrations approximately 5ppm in Co-Mo. Thus, Ni-Mo is more effective in saturating alkanes than Co-Mo.

Qualitative analysis of the liquid product showed that a large number of compounds were identified, however only a few major functional groups and respective compounds were quantified.

C. Gas Results

Quantification of the second stage non-condensable gases via the MRU online VARIOplus gas analyser took place at a detection temperature range of 25.9-27.5℃ with Heavy Fuel Oil (HFO) being the fuel type selected for the gas to be processed. For both Ni-Mo and Co-Mo the gas quality was similar. Typical CH_4 concentrations ranged between 220 to 3200ppm with the latter favoured at 350℃ and for a reaction time of 60 minutes. Typical concentrations for CO range between 20 to 304ppm, again with the latter favoured at 350℃ and for a reaction time of 60 minutes.

D. Physical Observations

A distinct colour change between the first and second stage liquid product was observed. Compared to the first stage, liquid product lighter in colour was obtained in the second stage.

No solid residue was formed in the second stage. Attrition of the Co-Mo and Ni-Mo catalyst particles was observed.

IV. CONCLUSION

In this study, evident in the GC-MS product distributions and physical observations of the process, the advantages of exploiting the two-step temperature-staged direct coal liquefaction process are demonstrated.

Co-Mo and Ni-Mo perform as suitable hydrotreating catalysts in upgrading the first stage liquid product, with Ni-Mo being the preferred HDS catalyst.

The second stage liquid has potential for application in the fuel industry as a diesel substitute or; as a solvent with a substantial BTX and aliphatic hydrocarbon quality.

Gas generated from the second stage of the process is rich in methane and carbon monoxide; and consideration should be given to its usefulness in providing energy as a heating medium; or recycled and used as syngas.

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