GAS EVOLUTION FROM THE PYROLYSIS OF JORDAN OIL SHALE IN A FIXED-BED REACTOR

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Abstract

Jordan oil shale from El-Lajjun deposit was pyrolysed in a fixed-bed pyrolysis reactor and the influence of the pyrolysis temperature between 400 to 620°C and the influence of the pyrolysis atmosphere using nitrogen and nitrogen/steam on the product yield and gas composition were investigated. The gases analysed were H_2, CO, CO_2 and hydrocarbons from C_1 to C_4. The results showed for both nitrogen and nitrogen/steam that increase the pyrolysis bed temperature from 400 to 520°C resulted in a significant increase in the oil yield, after which temperature the oil yield decreased. The alkene/alkane ratio including ethene/ethane, propene/propane, and butene/butane ratios, can be used as an indication of pyrolysis temperature and the magnitude of cracking reactions. Increasing alkene/alkane ratio occurring with increasing pyrolysis temperature. The alkene/alkane ratio for nitrogen/steam pyrolysis atmosphere was lower than the one found under nitrogen atmosphere.

Introduction

The world reserves of petroleum and natural gas are finite, although the years of oil and gas depletion are well into the future; there is much research into alternative sources of liquid hydrocarbons. Oil shales represent an enormous potential of liquid hydrocarbon reserves. For the potential to be maximised the conversion of the oil shale to oil should be undertaken as efficiently, economically and environmentally acceptable as possible. Therefore research investigations have concentrated on determining the process conditions which maximise the oil yield, however there are fewer data on the detailed analysis of the gases derived from pyrolysis of oil shale.

The main fixed-bed retorting variables under investigation are the maximum temperature, vapour residence time (the sweeping gas velocity), the particle grain size, shale residence time, and fluidising gas composition.

The use of steam in both fixed and fluidised bed in the pyrolysis of oil shale has been reported by many workers, for example, Carter and Taulbee [1], Dung and Udaja [2], Rothman [3], Braun and Chin [4], Raley *et al*. [5] and Wall [6].

It has been noticed that steam in oil shale pyrolysis could be a valuable pyrolysis gas in oil shale retorting for several reasons: 1) It has a high heat capacity and so would drive the retorting front more rapidly. 2) A higher heating value gas is left in the exit gas after the steam condensation. 3) A higher yield of hydrogen and CO that also raise the calorific value of the exit gas as a result of the reactions of the water–gas shift and char–steam reactions.

Kerogen pyrolysis, gas-phase, gas–solid secondary and mineral decomposition reactions affect the gas evolution profiles of oil shale pyrolysis. Campbell *et al*. [7, 8] and Huss and Burnham [9] investigated oil shale pyrolysis kinetics on the basis of the study of the evolution of H_2 and C_1 to C_4 hydrocarbon gases. Coburn [10] conducted a similar study with a limited number of gas species. The ratio of alkene to alkane gases in the evolved pyrolysis gases can be used to determine reaction mechanisms and indicate pyrolysis conditions. Burnham and Ward [11] investigated the reaction mechanisms that determine the observed alkene/alkane gas ratios under various conditions. Jacobson *et al*. [12] developed a retorting index (*RI*) which relates the ethene/ethane ratio to the retorting temperature. Campbell *et al.* [7, 8] developed relationships between ethene/ethane and propene/propane ratios and the logarithm of the heating rate during retorting for the non-isothermal pyrolysis of oil shale. They also compared this ratio for cracking and coking reactions and showed the relationship of their cracking studies to the 'retorting index' of Jacobson *et al*. [12]. Raley [13] interpreted data cracking from an oil shale pilot retort in terms of the chemical reaction mechanisms; he also found a relationship between the loss of oil yield and integrated values of the ethene/ethane ratio. Burnham and Taylor [14] related the ethene/ethane ratio to the temperature at which shale oil cracking occurred. Williams and Nazzal [15] reported alkene/alkane ratios, include ethene/ethane, propene/propane, and butene/butane ratios, that can be used as an indication of pyrolysis temperature. Raley [13] also showed that propene/propane ratios have a similar relationship to cracking and oil yield loss.

In this paper oil shale was pyrolysed in a fixed-bed pyrolysis reactor using both nitrogen and nitrogen/steam as sweeping gas. The influence of temperature between 400 and 620°C were also investigated. The pyrolysis parameters were studied in order to determine their effect on pyrolysis gas yield and composition.

Experimental

Oil shale

The oil shale sample was obtained from El-Lajjun deposit, south of Jordan. The oil shale was crushed to grain size of 1.20–3.33 mm and stored in the laboratory under dry conditions. The sample lithology and its general characteristics is described by Nazzal *et al*. [16].

Fixed-bed pyrolysis reactor

The fixed-bed reactor consisted of 200 cm³ stainless steel reactor externally heated by an electric rig furnace. The pyrolysis temperature, heating rate, shale residence time were controlled automatically. The sweeping gas was in the first part nitrogen which was pre-heated to 400°C, and nitrogen/steam at a ratio of 30:70 were together in the second part of the work. The liquid condensers consisted of glass linear contained within a cold trap, maintained at 0°C. The non-condensable gases were sampled at known time intervals over an experimental run. The gas samples were analysed using gas chromatography (GC), for the hydrocarbons gases from C_1 to C_4, CO, CO_2, H_2. The N_2 gas is used as a reference gas.

The pyrolysis temperature was maintained by the use of separate external heaters for the fixed-bed and the temperature was monitored at several points throughout the system. The pyrolysis temperature investigated were 400, 450, 520, 570 and 620°C. The flow rate of sweeping gas was altered to maintain the constant vapour residence time of 30 s. The experiment began by placing the crushed oil shale sample, 1.23–3.33 mm gain size, in the reactor and was then heated to 110°C and held at this temperature for 20 min to make sure that the samples were dry. The sample was heated at constant heating rate of 10°C min⁻¹ to fixed pyrolysis temperature varied from 400 to 620°C. The shale residence time at the maximum temperature was 30 min. The pyrolysis vapours were cooled in a series of water condensers, followed by condensation of the oils in a series of cold traps, maintained at different temperatures with the aid of ice/water, solid CO_2/methanol mixtures. The superficial residence time of the gases in the reactor was between 25–30 s depending on the pyrolysis temperature that included gas flow through the reactor. The resi-
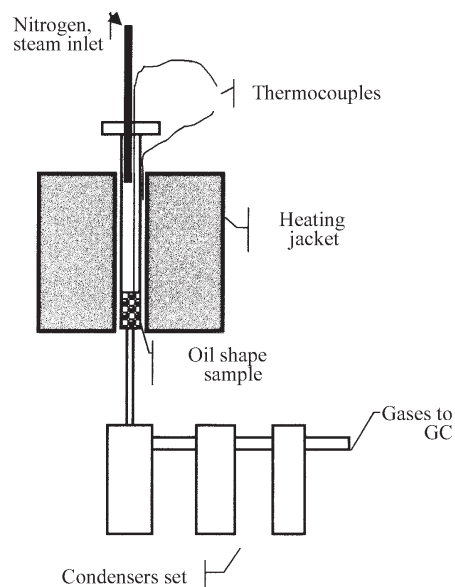
Fig. 1 The schematic diagram of the fixed-bed reactor

dence time would vary as pyrolysis vapours were evolved from the oil shale. Figure 1 shows a schematic diagram of the fixed-bed reactor.

Gas analysis

The evolved gases were sampled using a gas syringe at intervals throughout the duration of the pyrolysis of the oil shale and analysed off-line by packed column gas chromatography. The gases analysed were, CO, H_2 and CH_4, using a molecular sieve SA 60–80 column with argon as the carrier gas and a thermal conductivity detector. Nitrogen that was the purge gas used in the reactor was also determined on this column and the volumetric flow rates of the other gases were calculated by comparison with the nitrogen flow rate. CO_2 was determined separately using a silica gel column and argon as the carrier gas with a thermal conductivity detector. Gaseous hydrocarbons up to C_5 were determined on a Porasil C80–100 column with nitrogen as the carrier gas, using a flame ionisation detector.

Results and discussion

Products yield

The influence of pyrolysis temperature on oil yield and total gases using nitrogen and nitrogen/steam-sweeping gas are shown in Fig. 2. The oil yield increased from 1.5 to 8.85 mass% and from 2.2 to 9.8 mass% as the temperature was increased from 400 to 520°C for nitrogen and nitrogen/steam pyrolysis, respectively. Increase in temperature reduced the oil yield and reached a yield of 6.9 and 7.5 mass% at 620°C for nitrogen and nitrogen/steam respectively. These results show that oil yields obtained under nitrogen/steam atmosphere are higher by 111% of that obtained under nitrogen. At the pyrolysis temperature of 520°C, Carter and Taulbee [1] found that the oil yield obtained from the fluidised bed pyrolysis of oil shale using steam were only about 2.0 mass% higher than those obtained with nitrogen pyrolysis. The low oil yield at the bed temperature of 400°C was due to incomplete pyrolysis. Carter and Taulbee [1] showed that for the pyrolysis of Kentucky oil shale, USA, the maximum oil yield was produced at about 525°C for both nitrogen and nitrogen/steam pyrolysis. They suggest that the primary variable determining oil yield and composition in the pyrolysis of oil shale was the pyrolysis temperature. The rapid heat-up of the small oil shale particles quickly pyrolysis the kerogen forcing the volatile hydrocarbon products to more rapidly exit the particle, thereby decreasing the time for secondary reactions to occur. Once outside of the particle, the products are quickly swept from the pyrolysis zone reducing secondary degradation reactions. The maximum oil yield found which occurred at approximately 520°C is most probably due to two competing reactions. Increasing the pyrolysis temperature up to 520°C results in an increase in the particle heating rate, thereby enhancing mass transfer, shortening product residence time within the particle and consequently increasing oil yield [15]. However, higher bed temperatures are accompanied by increased coking and vapour cracking reactions.
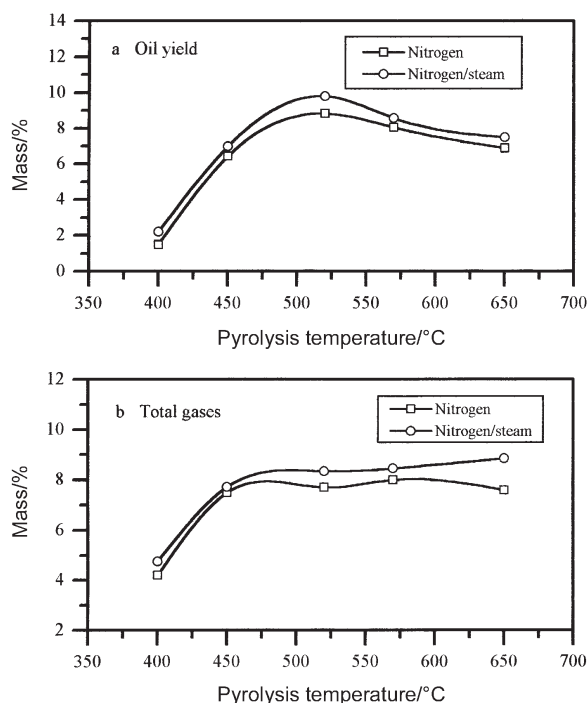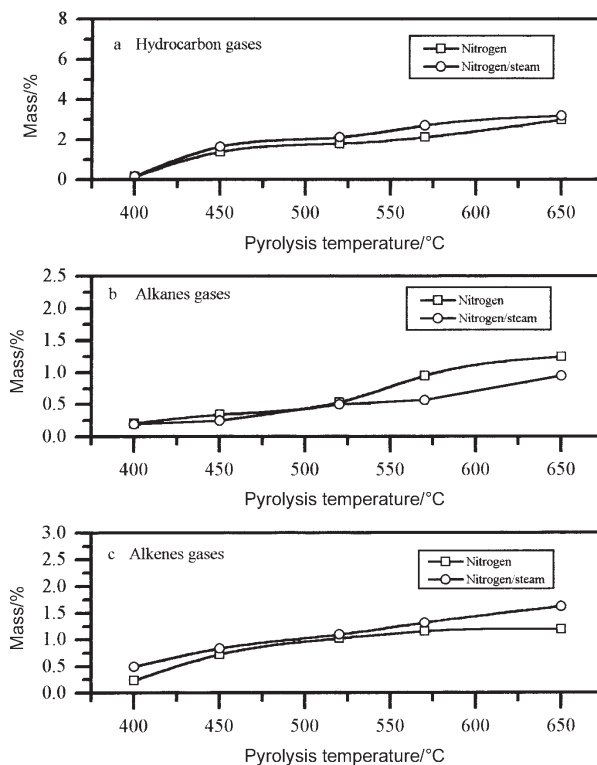
Fig. 2 The products yield of a – oil and b – total gases of oil shale pyrolysis in
fixed-bed reactor in the presence of nitrogen and nitrogen/steam

Therefore, at lower pyrolysis temperatures an incremental rise in temperature results
in an increase in liquid hydrocarbons yield, while at higher pyrolysis temperature, in-
creased oil degradation reactions become the limiting factor resulting in decreased oil
production [1].

Gas composition

Detailed analysis of the gas composition from the pyrolysis of oil shale revealed. The
main gases were hydrogen, carbon monoxide, carbon dioxide, methane, ethane, eth-
ene, propane, propene, with lower concentration of *iso*-butane, butane and butene has
been reported by many authors, for example, Campbell *et al*. [8] and Oh *et al*. [17]. In
all cases for nitrogen and nitrogen/steam pyrolysis, as the pyrolysis temperature was
increased, the mass percentage of the total gases and the hydrocarbon gases also in-
creased as shown in Figs 2b and 3a respectively.

Increasing the maximum pyrolysis temperature from 400 to 620°C caused in-
creases in the alkanes and alkenes in the derived gases from 0.21 to 1.25 and from
0.05 to 1.5 mass% in the nitrogen pyrolysis atmosphere, respectively.

Fig. 3 The products yield of a – H–C gases, b – alkanes gases and c – alkanes gases of oil shale pyrolysis in fixed-bed reactor in the presence of nitrogen and nitrogen/steam

But in the presence of steam, alkanes and alkenes concentration were increased from 0.2 to 0.95 and from 0.1 to 1.55 mass% by increasing the temperature from 400 to 620°C, respectively. The ethene to ethane ratio has been suggested as an indicator of oil shale retorting conditions, in particular the pyrolysis temperature [12]. The method has been applied to many oil shale pyrolysis research and extended to propene/propane and butene/butane ratios [13, 15]. The ratios of ethene/ethane, propene/propane, and butene/butane are shown in Figs 5a, b and c respectively. Carter and Taulbee [18] have suggested that the increase in the ratio with increasing pyrolysis temperature reflect the increase in secondary cracking reactions. Raley [19] has suggested a mechanism to explain the correlation of the ratio with heating rate as a free radical, chain reaction scheme. The dependence of alkene/alkane value on heating rate is attributed to the competition between carbon–carbon bond cleavage *vs*. hydrogen atmosphere processes. Figure 4 confirms that the alkene/alkane ratio, including ethene/ethane, propene/propane, and butene/butane ratios can be used as an indicator of pyrolysis temperature, increasing alkene/alkane ratios occurring with increasing pyrolysis temperature. These ratios increased with higher temperature illustrating the increase of cracking reactions. These ratios are higher for nitrogen/steam
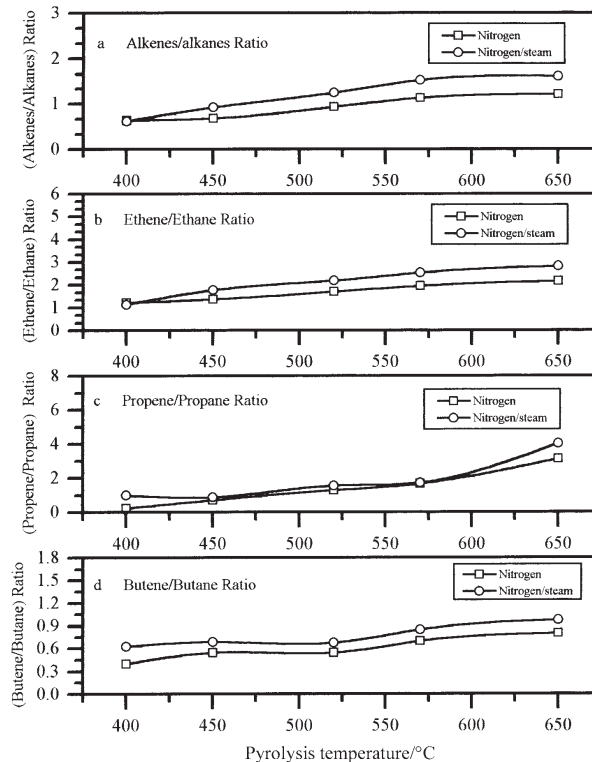
Fig. 4 The ratios of a – alkenes/alkanes, b – ethene/ethane, c – propene/propane and butene/butane gases evolved from the pyrolysis of oil shale in fixed-bed reactor

retorting, this suggests that the presence of steam played a role in the hydrocarbon gas formation mechanism. These results differ from the results of Carter and Taulbee [18] who reported that steam played little or no role in hydrocarbon gas formation.

The evolution of the methane and butene gases from the room temperature to the final pyrolysis temperature of 620°C at 10°C min^{-1} heating rate with shale residence time of 60 min under nitrogen and nitrogen/steam pyrolysis atmosphere are shown in Fig. 5, respectively. It was not possible to determine the exact temperature of the maximum evolution, because the gas sampling was off-line at different pyrolysis times. Methane reached a maximum evolution between 450 and 550°C. But for butene the maximum evolution was lower by 50°C than that of methane. This result agree with that reported by Oh *et al.* [17] were the higher MW hydrocarbon gases are produced at a lower maximum temperature than the lower MW species. The presence of steam caused an increase of the gas evolution for both methane and butene and a shift toward a higher temperature of the maximum evolution around 50°C.
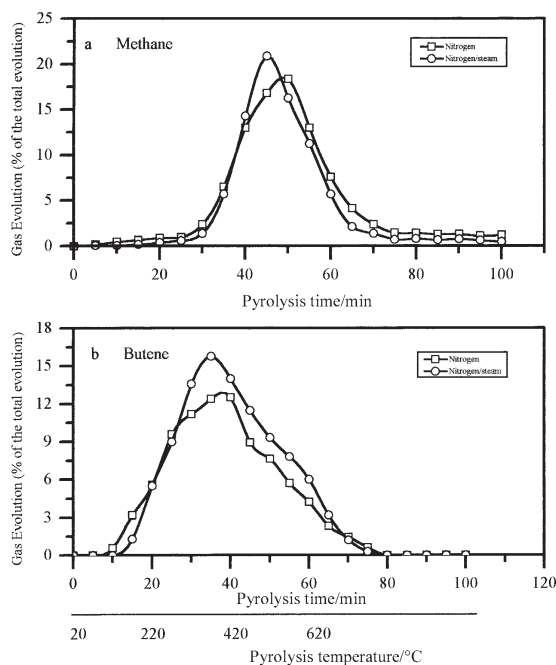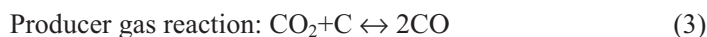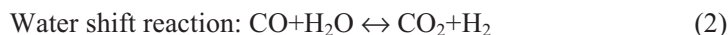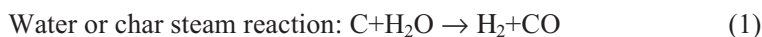
Fig. 5 Gas evolution of a – methane and b – butene during oil shale pyrolysis in fixed-bed reactor at 10°C min^{-1} heating rate in nitrogen and nitrogen/steam atmosphere
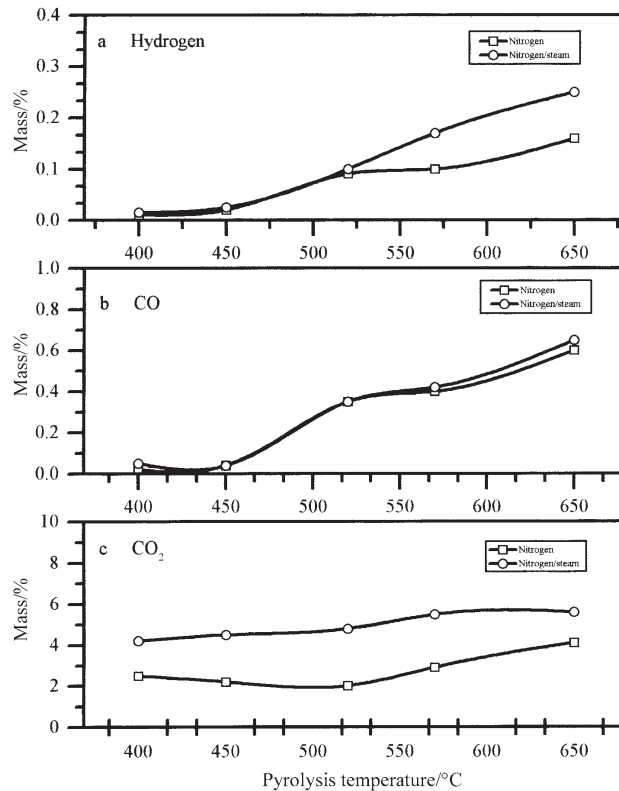
H$_2$, CO and CO$_2$

The notable difference in the gas compositions using nitrogen and nitrogen/steam in the fixed-bed is the amount of hydrogen and CO$_2$ produced as shown in Figs 6a and 6b, respectively. At the pyrolysis temperature of 520°C, H$_2$ evolution increased from 0.10 to 0.16 mass%. CO$_2$ evolution increased from 2.50 to 4.10 mass%. It is apparent that the yield of hydrogen was larger under nitrogen/steam pyrolysis than under nitrogen pyrolysis. In all cases, the presence of steam in the retorting atmosphere markedly increased the mass percentage of CO$_2$ in the product gas stream as shown in Figs 6a, and 6b. It is also apparent that CO production generally is less for the nitrogen pyrolysis compared to that of the nitrogen/steam pyrolysis as shown in Fig. 6c.

A comparison of the yields of H$_2$, CO, and CO$_2$ in the various atmosphere and different pyrolysis temperature shows the effects of the following reactions:

$$\text{Water or char steam reaction: } C+H_2O \rightarrow H_2+CO \tag{1}$$

$$\text{Water shift reaction: } CO+H_2O \leftrightarrow CO_2+H_2 \tag{2}$$

$$\text{Producer gas reaction: } CO_2+C \leftrightarrow 2CO \tag{3}$$

$$\text{Mineral carbonate decomposition: } MCO_3 \rightarrow MO+CO_2 \tag{4}$$

$$\text{Hydrocarbons–steam reaction: } 2HC+H_2O \rightarrow O_2+CH_4 \tag{5}$$

Fig. 6 Gas evolution of a – hydrogen, b – carbon monoxide and c – carbon dioxide of oil shale pyrolysis in fixed-bed reactor

In those runs carried out in a nitrogen atmosphere, reaction (1) occurs to some extent due to water production in front of the retorting zone in the temperature range from 450 to 500°C. At the same time, reactions (1) and (2) may or may not occur. As water production and mineral carbonate decompositions are increased, by increasing the temperature, they would force the equilibrium of reactions (2), (4), and (5) to the right. But in the nitrogen/steam runs, steam was injected into the reactor where it reacted with the carbonaceous residue and the CO_2 was produced through reactions (2), (4), and (5). As the temperature of the oil shale pyrolysis exceeds 500°C, carbonate minerals in the oil shale begin to decompose and calcite $CaCO_3$ and ankeritic dolomite $(Mg,Fe)Ca(CO_3)_2$ are the carbonate minerals of interest. Burnham [20] has found that the carbonate and resulting oxides react with the quartz to form silicates and silicate products that are more stable. Burnham [20] and Campbell [21] show the rate of decomposition of the carbonates and the rate of silicate formation that depend on the gas environment. They show that dolomite decomposition in nitrogen atmosphere takes place with a one-step decomposition reaction at 675°C as shown in the following reaction.

$$CaMg(CO_3)_2 \leftrightarrow CaO+MgO+2CO_2$$

with an enthalpy of CO_2 liberating reaction is 401 cal (g carbonate)$^{-1}$.

While in steam atmosphere the decomposition takes place in two steps: first step dolomite decomposition:

$$CaMg(CO_3)_2 \leftrightarrow MgO+CaCO_3+CO_2$$

and the second step the calcite $CaCO_3$ reacts with quartz SiO_2 to produce silicates:

$$CaCO_3+SiO_2 \leftrightarrow Silicates+CO_2$$

With an enthalpy change of CO_2 liberation is 171 cal (g carbonate)$^{-1}$ and 201 cal (g carbonate)$^{-1}$ for step 1 and step 2 respectively [20, 21].

Conclusions

1. Oil shale has been pyrolysed in both nitrogen and nitrogen/steam atmosphere to the pyrolysis temperature varied from 400 to 620°C.

2. Increasing the pyrolysis temperature from 400 to 520°C resulted in a large increase in the oil yield from 1.5 to 8.85 mass%, from 2.2 to 9.8 mass%, for nitrogen and nitrogen/steam fluidisation, respectively. After which temperature, there was a decrease in oil yield for both atmospheres. Therefore steam-sweeping gas can potentially produce oil yields as much as 111% of that of nitrogen atmosphere.

3. A large increase in the yield of hydrocarbon gases occurred as a result of increasing the pyrolysis bed temperature from 520 to 620°C which was attributed to an increase in thermal cracking of pyrolysis vapours.

4. Nitrogen/steam retorting produced markedly higher concentration of CO_2, H_2 and hydrocarbon gases and similar CO concentration to those using nitrogen retorting. Hydrogen in the outlet gas was considerably increased by the steam-char and water gas shift reactions.

5. Alkene/alkane ratios including ethene/ethane, propene/propane, and butene/butane ratios can be used as an indicator of pyrolysis temperature; increasing alkene/alkane ratios occurring with increasing pyrolysis temperature.

6. Alkene/alkane ratios generally can be taken as an indicator of the magnitude of cracking reactions for both nitrogen and nitrogen/steam sweeping gas pyrolysis.

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