Composition of gas from pyrolysis of Estonian oil shale under N₂ and CO₂

Sepehr Mozaffari*¹, Oliver Järvik, Zachariah Steven Baird

Department of Energy Technology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

Abstract

Studying the evolution of gas during the decomposition process of oil shale provides information about the changes of gas composition and understand the mechanism of pyrolysis process. A few number of studies focused on using CO₂ atmosphere to observe the effect of sweep gas on pyrolysis products. Fischer assay method was used to analyze the pyrolysis of Estonian kukersite oil shale under CO₂, CO₂/steam, N₂ and N₂/steam. The gaseous products were collected offline using a sample bag. Gas chromatography was performed to investigate the evolution of C₁-C₃ gases, H₂, CO₂ and CO. Subsequently, the results from each test were analyzed and compared. Our results show that in comparison with N₂, pyrolysis in CO₂ increased the production of alkanes and hydrocarbon gases. Also, generation of CH₄ and CO gases were enhanced under CO₂, while composition of H₂ did not significantly change in the gaseous products for both environments. For the tests in presence of steam, the results show that unlike the N₂ atmosphere, CO₂/steam decreased the production of total hydrocarbons, H₂, CO₂ and CO.

Keywords: oil shale, fischer assay, pyrolysis, steam, gas evolution, CO₂, N₂

* Corresponding author: email sepehr.mozaffari@taltech.ee

1.Introduction

Among the energy sources such as coal, oil shale and biomass, oil shale is considered to have great potential due to the large size of the known deposits [1]. Therefore, oil shale can be an alternative fuel to be used as an energy source. Also, oil shale utilization could keep the balance between energy production and consumption, ensure energy security and benefit countries economically [2]. As a result, production of energy from oil shale has been used by several countries to supply and meet their energy demands.[3] For instance, Estonia has been generating energy to meet their domestic needs from shale oil by producing heat, electricity and power as well as diesel fuel while only 1.1% of the world reserves exist in Estonia. [4] However, the continual use of fossil fuels causes an increase in emission of greenhouse gases into the environment, which leads to climate change [5]. Studying various aspects of the processing of oil shale would be helpful to assess and mitigate the environmental risks [6]. In light of these reasons, investigating alternative fuels has raised interest among researchers and accordingly, abundant analysis has been done on shale oil derived from pyrolysis. However, detailed data and analysis of the shale gas from pyrolysis seems to be rare. Gas yields and compositions are important parameters to learn about the potential quality of the shale gas produced. Data on shale gas can be helpful to give better understanding about the chemistry related aspects of gas and oil formation [7]. This, in fact, depends on many factors such as the final temperature, residence time, heating rate, production approach applied, oil shale characteristics, condenser and so on. Since decomposition of kerogen and conversion to oil takes place mainly at temperatures below 500°C, studying the evolution of gas gives more information about the gas composition as well as the mechanism of the decomposition process. The analysis of oil yield was provided in the first part of study.

In this paper the compositions of H₂, CO, CO₂, and C₁-C₃ hydrocarbons in the gaseous product, and also the evolution of these gases at different temperatures during the pyrolysis are reported. These results provide insights about the release of these gases and their dependency on temperature.

2. Experimental section

2.1. Fischer assay

A kukersite oil shale sample from the Ojamaa mine located in northeast Estonia was obtained to conduct the pyrolysis experiments. A Fischer assay retort was used to carry out the pyrolysis. 50 g of the oil shale sample was crushed to a particle size of 500-710 μm . The pyrolysis test was conducted under CO_2 , CO_2/steam , N_2 and N_2/steam . The pyrolysis gases were introduced into the retort at 21 ml/min and for the steam tests the gas and water flow rates were 10 and 0.1 ml/min. The sweep gases were injected into the system one hour earlier before the pyrolysis began to ensure the air was totally flushed out of the retort. Then, the retort was heated up to 500 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, to 520 $^{\circ}\text{C}$ at 1 $^{\circ}\text{C}/\text{min}$ and held at 520 $^{\circ}\text{C}$ for 20 minutes. The total run was carried out in 90 min. For the tests with steam, a small heater was used to convert the injected water into steam before it reached the retort.

2.2 Gas chromatography

A Shimadzu GC-2014 gas chromatograph with a thermal conductivity detector and a valve system was used to analyze the various gases in a single run. O_2 , N_2 , and CO , were analyzed using a 3 m packed column with 5 $\text{\AA}$ molecular sieves (OD 1/8", ID 2 mm, 80/100 mesh) and a 9 m 25% DC-200/Shimalite packed column (60/80 mesh, OD 1/8", ID 2 mm) was used to analyze the CO_2 . Determining the amount of the aforementioned gases was possible by calibrating. Calibration of the GC was done by injecting 3 ml of gas with different compositions of O_2 , N_2 , CO and CO_2 . The temperature for the column oven program started from 35 $^{\circ}\text{C}$ (held isothermally for 3 minutes), followed by heating until 85 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$ (also held isothermally for 3 minutes), and finally a ramp up to 125 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$. The total time was 20 min. The injector temperature was 250 $^{\circ}\text{C}$ and the split ratio was 10:1. Also, a Gazohrom-3101 gas chromatograph with a thermal conductivity detector (GC-TCD) was used to analyze the compositions of H_2 , CO and CH_4 . Air with a flow rate of 65 mL/min was used as the carrier gas to determine the compositions of H_2 , CO , CH_4 . Also, a packed

column (ID 3.5 mm, length 2.5 m), which operated at room temperature, was used for separation. The injection volume was 2 mL and the relative standard deviation for parallel measurements for the GCs did not exceed 10% and 5% respectively. In Shimadzu GC-2014, Peaks for larger hydrocarbons could also be observed. Calibrations were not available for these compounds, so to determine the compositions of C₂ and C₃ hydrocarbons from their peak areas, the CH₄ peak area from Gazohrom was used as a reference and the ratio of the thermal conductivities was used to account for the different properties of the gases. To calculate the composition of C₂ and C₃ hydrocarbon gases, it was assumed that peak areas are directly proportional to thermal conductivity of the compounds at corresponding temperature. Although this leads to a somewhat higher uncertainty, it also allowed us to obtain information on the concentrations of these compounds that would have otherwise been lost. Consequently, the gas composition values for these compounds would rather provide qualitative data with gas trends throughout the experiment.

3.Results and discussion

3.1 Gas analysis

Table 1 and 2 present the detailed analysis of gas compositions at different test temperatures and atmospheres and how they evolved during the pyrolysis as a function of temperature. The main gases analyzed were H₂, CO, CO₂, and C₁-C₃ hydrocarbons.

Table 1 Gas compositions at different phases of the Fischer Assay test under N₂ and N₂/steam

Gas composition, %	N ₂				N ₂ /steam			
	200-400 °C	400-500 °C	500-520 °C	520 °C	200-400 °C	400-500 °C	500-520 °C	520 °C
CO	0.2	5.1	5.1	1.8	0.1	5.2	5.1	2.4
CO ₂	2.3	12.3	10.7	5.8	1.3	17.0	14.9	16.2

H₂	0.0	1.3	4.9	4.7	0.0	1.6	4.5	2.7
CH₄	0.4	3.5	16.4	11.7	0.5	7.0	19.1	11.1
C₂H₄	0.0	0.7	2.3	0.9	0.0	1.3	2.6	1.0
C₂H₆	0.0	1.9	7.7	3.0	0.0	4.3	8.7	3.0
C₃H₆	0.0	2.5	3.4	0.9	0.0	6.8	5.0	2.1
C₃H₈	0.0	1.6	5.5	1.8	0.0	3.6	6.3	1.9
Total HC gases	0.4	10.1	35.3	18.3	0.6	23.0	41.8	19.2
Alkanes	0.4	7.0	29.7	16.5	0.5	14.8	34.1	16.1
Alkenes	0.0	3.1	5.7	1.7	0.0	8.1	7.6	3.1
Alkenes/Alkanes ratio	0.1	0.4	0.2	0.1	0.0	0.5	0.2	0.2

Table 2 Gas compositions at different phases of the Fischer Assay test under CO₂ and CO₂/steam

	CO ₂				CO ₂ /steam			
Gas composition, %	200-400 °C	400-500 °C	500-520 °C	520 °C	200-400 °C	400-500° C	500-520 °C	520 °C
CO	0.1	7.9	7.7	2.9	0.4	6.2	5.0	2.8
H₂	0.0	1.8	4.7	3.6	0.0	1.3	4.6	4.4
CH₄	0.4	8.2	16.0	11.9	0.4	5.5	18.8	18.1
C₂H₄	0.1	1.6	4.8	0.7	0.2	1.2	3.0	2.0
C₂H₆	0.1	5.1	16.3	2.0	0.1	3.8	9.5	5.6
C₃H₆	0.0	5.7	7.8	0.0	0.0	7.5	7.1	4.4
C₃H₈	0.0	4.0	11.2	0.5	0.0	3.4	7.2	4.1
Total HC gases	0.6	24.6	56.2	15.1	0.8	21.5	45.6	34.2
Alkanes	0.5	17.3	43.5	14.3	0.6	12.7	35.5	27.8
Alkenes	0.1	7.3	12.7	0.7	0.2	8.8	10.1	6.4
Alkenes/Alkanes ratio	0.2	0.4	0.3	0.1	0.4	0.7	0.3	0.2

Campbell et al. [33] studied oil shale pyrolysis mechanisms from 25 °C to 900 °C and described oil shale pyrolysis as a simplified two-step process of kerogen to bitumen and bitumen to oil. In addition, they suggested that only small amounts of non-condensable gases are produced during the process of conversion of kerogen to bitumen; however, during the conversion of bitumen to oil, evolution of non-condensable gases takes place [8]. This also can be found in this work as seen from Table 1. Only traces of non-condensable gases were produced before 400 °C and above this temperature up to 500 °C the main evolution of oil and gas can be observed.

The detailed analysis of evolved hydrocarbon gases during the pyrolysis as a function of temperature and the presence of steam is shown in Figures 1-3. As shown in the figures, in all test environments total HC gases, alkanes and alkenes were increased by increasing the retort temperature. Moreover, these figures indicate that steam caused an increase in the concentration of hydrocarbon gases, alkanes and alkenes in the gaseous products for the nitrogen atmosphere. These results agree with several other researchers' works [9]–[11]. Nazzal [12] suggested that the presence of steam in oil shale pyrolysis could play an important role on the exit gas composition because in addition to having a high heat capacity, steam speeds up the pyrolysis process. Also, steam increases the heating value of gaseous product after condensation as a result of increase in concentrations of CO and H₂.

Figure 1 Relative distribution of hydrocarbon gases produced

Figure 2 Evolution of alkane gases

Figure 3 Evolution of alkene gases

However, looking at the graphs more closely, it seems that steam has the opposite effects when injected into N₂ and CO₂ environments. In an N₂ atmosphere, steam enhanced the total amounts of HC gases, alkanes and alkenes. These results agree with Nazzal's findings where a small increase in total HC gases and alkenes and a slight difference in alkanes production was observed between 400 °C and 520 °C in the nitrogen/steam environment [12]. As stated earlier, the results show a different effect for steam in a CO₂ atmosphere. In CO₂, steam caused a decrease in total hydrocarbon and alkane gases production; however, the presence of steam initially increased the concentration of alkene gases (up to 400 °C), and then reduced it as evolution of oil began to occur (450 °C). Subsequently, steam seemed to decrease the concentration of alkenes at higher temperatures.

Table 1 also shows the alkenes/alkanes ratios for all tests during the HC gases evolution. The ratio of alkenes to alkanes has been used to determine reaction mechanisms and indicates pyrolysis conditions [11], [13]. Several researchers have suggested that an increase in the alkene/alkane ratio is a result of secondary cracking reactions [9], [11], [12] and lower ratios are associated with coking reactions [1], [2]. The results for the alkene/alkane ratio show that initially the ratio increased and then decreased during pyrolysis. The highest values for the alkene/alkane ratio can be due to the occurrence of secondary gas phase reactions in the temperature range of 400 °C to 500 °C where

oil and gas evolution largely takes place. Moreover, these ratios were mostly higher for the pyrolysis with steam. Williams and Nazzal [9] suggested that even though steam increases the oil yield by decreasing the secondary coking reactions it also increases the alkene/alkane ratio, meaning an increase in the secondary vapor phase cracking reactions.

Figure 4 exhibits the evolution of CO₂ in the gas products during pyrolysis in N₂ and N₂/steam. Even though studying CO₂ evolution for the tests in CO₂ was not possible, such measurements were made for the N₂ and N₂/steam environments. It can be seen from the figure that the yield of CO₂ was greatly increased under the run with steam. This could be as a result of various reactions such as the water-gas shift reaction, mineral carbonate decomposition reactions as well as steam-hydrocarbon reactions. By increasing the pyrolysis temperature, decomposition of mineral carbonates and production of water increases, which leads to higher production of CO₂ [12]. Looking at the yield of gases throughout the pyrolysis process (up to 500 °C) indicates that CO₂ made up the largest portion of the gaseous products. This may suggest that water vapor plays a role in oxidation reactions.

Figure 4 CO₂ evolution as a function of temperature

William and Nazzal [12] related the higher gas yield in N₂/steam to the higher CO₂ concentration that is produced at higher temperatures and suggested that this is coupled with a series of reactions, namely the char-steam, water gas-shift, hydrocarbon steam and mineral carbonate-steam reactions.

Figures 5-7 compare the yields of CO and H₂ and CH₄ during the decomposition of kerogen. Since the gas sampling was offline, it was not possible to find the precise peak temperature where the evolution of gas takes place. From the figures it can be perceived that the peak for carbon monoxide, hydrogen and methane evolution occurs at around 400-450 °C, 480-510 °C and 500 °C, respectively. Huss and Burnham [14] also studied the gas evolution of different shale samples during pyrolysis in a reactor under argon over a temperature range of 25-950 °C at the heating rate of 2 °C/min. Their findings show that CO, H₂ and CH₄ evolution mostly happens at 425-435 °C, 465 °C and 480-520 °C, respectively. They associated this phenomenon with oil generation which occurred at the maximum rate at 430-435 °C.

Figure 5 Evolution of CO during kerogen decomposition

Figure 6 Evolution of H_2 during kerogen decomposition

The experimental results showed that in the presence of steam CO starts to be produced at around 400 °C and has its highest content when the oil is about to be generated. It appears that the concentration of CO in nitrogen pyrolysis is lower than that in nitrogen/steam. That is partially because of the reactions that the produced water and injected steam initiate with the char to produce hydrogen and carbon monoxide. Also, in the water gas shift reaction, steam and CO produce hydrogen and CO_2 . These reactions seem to have an effect on the compositions of CO and H_2 in the retort. In addition, at higher temperatures, the CO composition is reduced and hydrogen increased. Also, it appears from the results in nitrogen that using CO_2 as a sweep gas significantly increased the amounts of CO and H_2 in the gaseous products. Generally, it was observed that steam injection into a CO_2 atmosphere lowered the yields of H_2 and CO in the produced gas and increased them in the nitrogen environment.

Figure 7 Evolution of CH₄ during kerogen decomposition

Comparison of methane evolution in the products indicates that CH₄ formation is higher in a CO₂ atmosphere than in N₂. It is apparent that the presence of steam yielded higher methane concentrations in N₂ at all temperatures while in CO₂ methane formation only increased at higher temperatures. This can be explained by the following reaction between steam and hydrocarbon gases in which oxygen and methane are formed. For this reason, the yield of methane in pyrolysis with steam is higher.

It is worth noting that a sharp increase can be observed from about 400 °C onward. This is the approximate temperature when bitumen is converted to oil and shale oil generation begins. As explained before, as the temperature increased the total concentration of HC gases increased and consequently H₂ and CH₄ formation in the retort increased as well. During the last phase of the test (where the retort temperature was held at 520 °C for 20 minutes) and due to consumption of the shale sample over time, less hydrocarbons were produced and as a result methane formation decreased.

4. Conclusions

This research focused on gaseous products of the pyrolysis of Estonian kukersite oil shale under the Fischer assay method. The test was conducted in four different atmospheres; CO₂, CO₂/steam, N₂ and N₂/steam. Gas chromatography was used to measure the composition of all collected gases. The gas analysis showed that more hydrocarbon gases were produced when steam was injected in N₂. Conversely, the presence of steam caused a reduction in total hydrocarbon gases and alkane gases in a CO₂ atmosphere. Moreover, the results from CO₂/steam indicated that steam lowered the concentrations of H₂ and CO compared with the CO₂ atmosphere. Furthermore, the alkenes/alkanes ratio, which is used to determine reaction mechanisms, showed an initial increase followed by a decrease in the ratio. Analyzing and investigating the outcomes obtained from studying gas evolution could result in development and advancement of processes and technology to enhance the oil and gas yields.

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