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VALIDATION RESULTS FOR CORE-SCALE OIL SHALE PYROLYSIS

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Topical Report

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ABSTRACT

This report summarizes a study of oil shale pyrolysis at various scales and the subsequent development a model for in situ production of oil from oil shale. Oil shale from the Mahogany zone of the Green River formation was used in all experiments. Pyrolysis experiments were conducted at four scales, powdered samples (100 mesh) and core samples of 0.75", 1" and 2.5" diameters. The batch, semibatch and continuous flow pyrolysis experiments were designed to study the effect of temperature (300°C to 500°C), heating rate (1°C/min to 10°C/min), pressure (ambient and 500 psig) and size of the sample on product formation. Comprehensive analyses were performed on reactants and products - liquid, gas and spent shale. These experimental studies were designed to understand the relevant coupled phenomena (reaction kinetics, heat transfer, mass transfer, thermodynamics) at multiple scales.

A model for oil shale pyrolysis was developed in the COMSOL multiphysics platform. A general kinetic model was integrated with important physical and chemical phenomena that occur during pyrolysis. The secondary reactions of coking and cracking in the product phase were addressed. The multiscale experimental data generated and the models developed provide an understanding of the simultaneous effects of chemical kinetics, and heat and mass transfer on oil quality and yield. The comprehensive data collected in this study will help advance the move to large-scale in situ oil production from the pyrolysis of oil shale.

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1. Introduction

Energy is essential for the future success of the United States of America and other first world countries. There are a few criteria placed on this energy. The energy must be long-lasting, have low emissions, and be economical. Thus far, oil shale partially meets one of these criteria. Oil shale can be considered long-lasting, with an estimated 1.5 to 1.8 trillion barrels of shale oil in the Green River formation [1]. The other two criteria must be met through advances in technology (i.e., in situ retorting) and higher prices for crude oil due to supply and demand. This report focuses on the technology portion of the criteria to make oil shale a usable resource.

Different in situ technologies have been proposed for commercial oil shale development. Royal Dutch Shell built a pilot scale InSitu Conversion Process (ICP) [2]. The technology involved in ExxonMobil's ElectroFracTM process was presented at the 26th Oil Shale Symposium [3]. Chevron's CRUSH process was patented in 1979 [4]. Each method varies in implementation, but the underlying physical restraints of kinetics, thermodynamics, heat transfer, and mass transport must be overcome.

Simulating the differences between in situ and ex situ retorting will enable experts in the field to compare the different technologies economically and environmentally (emissions). In order to predict what might occur far beneath the ground, simulation tools must be validated against available experimental data, including ex situ retorting data. Tiwari performed the initial steps in the validation process with a thermal gravimetric analysis (TGA), high pressure TGA (HPTGA), TGA with mass spectrometry (TGA-MS), and multiscale pyrolysis on different sizes of core samples [5].

In this report, experiments were performed to determine effects of four factors on products from oil shale pyrolysis: core size, heating regime, pressure, and temperature. In these experiments, the magnitude of the effect of each factor on the oil production was determined. It was shown that each of the four factors contribute to oil yield and product distribution. These factors may be used in enhancing the techniques that exist for oil shale pyrolysis.

2. Physical Phenomena of Model

There are four physical phenomena that need to be addressed to optimize in situ and ex situ pyrolysis. One, heat transfer through the oil shale will be the key to unlocking the oil from the oil shale in an economical manner. Two, reaction kinetics will show the optimum heat regime for maturing the kerogen into oil. Three, mass transfer will move products of the matured kerogen through the rock to a recoverable area. Four, thermodynamics will affect each of the other phenomena; as the products are formed, their properties will change. Each of these phenomena is affected by the nature of the rock and the kerogen, the type of heat source used, the pressure of the system, and the time the rock is at a given set of conditions.

In the present work, models have been developed to represent each of the four important phenomena associated with oil shale pyrolysis [5]. These models are validated through experiments such as TGA and multiscale pyrolysis. Extrapolating these models from a controlled experiment to an underground reservoir has inherent risks. One major risk is that heat and mass transfer pathways are likely to develop during large-scale pyrolysis, and the homogeneous model determined from the sample size cannot accurately describe these pathways.

3. Oil Shale Pyrolysis Experiments

Pyrolysis of oil shale occurs when the endothermic energy barrier is overcome. This energy barrier is overcome at approximately 300°C and the decomposition rate accelerates as the temperature increases [6]. While select results from the pyrolysis of powdered oil shale samples and oil shale cores are presented here, more detailed results can be found in “Oil Shale Pyrolysis: Benchscale Experimental Studies and Modeling” [5]. This report focuses on heat and mass transport effects in larger core samples.

This section describes how oil shale samples from the Green River formation were characterized, pyrolyzed, and post processed to obtain the results.

3.1 Oil Shale Characterization

Two sets of samples collected from the Mahogany zone of the Green River

formation were provided by the Utah Geological Survey (UGS). The samples were labeled Sample #1 (powdered oil shale (PO)) and Sample #2 (core oil shale (CO)). Sample #1 was only available in powdered form. Sample #2 came in four varieties, powdered, and 0.75", 1", and 2.5"-diameter cores. The samples were tested for inherent moisture and characterized using elemental analysis (CHNSO) and X-ray diffraction (XRD).

To test for inherent moisture, small quantities of Sample #1 and the powdered (100 mesh) form of Sample #2 were dried at 100°C for 4 hours. No significant weight loss was observed, so the samples were used as received.

CHNSO analysis was done to characterize the common elements of organic content of the oil shale using a LECO CHNS-932 for Carbon (C), Hydrogen (H), Nitrogen (N), and Sulfur (S) and a VTF-900 for Oxygen (O). Both Sample #1 and Sample #2 were located on a van Krevelen chart as type-1 kerogens by using the ratios O/C and H/C. The results of the elemental analysis are shown below in

Table 1. CHNSO results for the raw oil shale samples. H/C (molar) and O/C (molar) are calculated for kerogen typing.

CHNSO	Sample #1 (PO)		Sample #2 (CO)	
	Weight %	Stdev	Weight %	Stdev
Carbon	17.45	0.26	22.09	1.00
Hydrogen	1.60	0.08	2.14	0.12
Nitrogen	0.53	0.06	0.65	0.06
Sulfur	0.18	0.04	0.11	0.02
Oxygen	15.69	0.79	16.54	0.97
H/C (molar)	1.10	---	1.17	---
O/C (molar)	0.67	---	0.56	---

The samples' minerals were ground in a micronizing mill to 325 mesh then characterized using XRD. The mineral composition is important for determining the likelihood of TGA and multiscale pyrolysis results being affected by mineral reactions. The results of the XRD characterization are seen below in Table 2. While there are many constituents, dolomite (33.5 wt.% and 62.93 wt.% in Sample #1 and Sample #2, respectively) was the predominant mineral in both samples. Illite and analcime, found in both samples, may add to the complexity of modeling the reaction kinetics because

water is released from these minerals at a relatively low temperature. Other complexities to modeling the pyrolytic reactions are the emission of CO₂, O₂, and minerals as the rock degrades.

Table 2. Results from XRD of oil shale rock.

Minerals	Weight %		Chemical Formula
	Sample #1 (PO)	Sample #2 (CO)	
Quartz	7.7	7.7	SiO ₂
Plagioclase	19.5	7.60	CaAl ₂ Si ₂ O ₈
Calcite	6.9	3.95	CaCO ₃
Illite	5.8	2.84	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ .(H ₂ O)]
Dolomite	33.5	62.93	Ca Mg (CO ₃) ₂
Orthoclase	12.4	10.88	KAlSi ₃ O ₈
Aragonite	11.7	--	CaCO ₃
Analcime	2.4	4.13	NaAlSi ₂ O ₆ .H ₂ O

3.2 Experimental Procedures

Four different experimental procedures were employed to study the phenomena discussed in Section 2. These procedures were carried out on powdered and core samples as indicated. A summary of the experiments performed are shown below in Table 3.

1. TGA: Performed on Sample #1 and Sample #2 (powder) to obtain intrinsic reaction rates of the oil shale. Performed isothermal experiments from 200°C to 550°C (heating rate 100°C/min) and nonisothermal experiments with heating rates between 0.5°C/min and 50°C/min.
2. HPTGA: Performed on Sample #1 and Sample #2 (powder) to determine pressure effects on intrinsic reaction rates
3. TGA-MS: Performed on Sample #1 to determine at which temperature targeted components evolved
4. Multiscale Pyrolysis: Performed pyrolysis under batch, semibatch, and continuous reactor conditions on Sample #1 to determine secondary reaction parameters. Then, performed pyrolysis under continuous reactor conditions

on Sample #2 cores (0.75"–2.5" diameter) to compare transport resistances (mass and heat), and effects of pressure (ambient and 500 psig), core size (0.75"- to 2.5"-diameter), heating rate (1°C to 10°C), and final temperature (300°C to 500°C) on product yield and distribution.

a. Product post processing

- Gas chromatography (GC) and GC-MS: Characterized gas and oil using a single carbon number
- Elemental analysis
- Fourier transformation infrared spectroscopy (FTIR): Found the wax appearance temperature of the oil
- Densitometry: Found the density of the oil
- Rheometry: Found the viscosity of the oil

b. Spent shale post processing

- TGA-Differential Scanning Calorimetry (TGA-DSC): Used to find unreacted organic material and coke left in the rock
- Elemental analysis

Table 3. Oil shale samples and experimental procedures performed.

Oil Shale Sample	Size	Experimental Procedure
Sample #1	Powder	TGA HPTGA TGA-MS Multiscale Pyrolysis (1" Swagelok Reactor)
Sample #2	Powder 0.75" diameter 1" diameter 2.5" diameter	TGA HPTGA ----- Multiscale Pyrolysis (1.25" Swagelok Reactor) Multiscale Pyrolysis (1.25" Flange Reactor) Multiscale Pyrolysis (3.0" Flange Reactor)

3.3 TGA Pyrolysis Experiments

TGA measures changes in weight of a sample undergoing pyrolysis to indirectly

observe the progress of reactions. TA Instrument's Q500 was the TGA equipment used in these experiments. It was able to control the temperature of the reaction chamber up to a maximum temperature of 1000°C using electrical heating, to accommodate sweep/reacting and balance gases with a total flow rate of 100 ml/min, and to provide heating rates from 0.1°C/min to 100°C/min. When the TGA was coupled MS, a Thermostat model GSD 301 TC from Pfeiffer Vacuum MS was used. HPTGA was performed using the Cahn TherMax 500 High-Pressure TGA from Thermo Fischer to study the pressure effects on the intrinsic kinetics and product distribution.

The TGA was purged with nitrogen (N₂) for 15 minutes prior to initiating the experiment. Approximately 20 milligrams of Sample #1 or powdered (100 mesh) Sample #2 was placed in a platinum basket attached to a microbalance with a small wire. Mass or heat transport effects were assumed to be negligible because of the size of the particles. The reactor was then heated to the desired temperature at a set heating rate. The balance gas (N₂) was maintained at 40 ml/min and 10ml/min and the purge gas at 60 ml/min and 90 ml/min for the TGA and TGA-MS experiments, respectively.

3.4 Multiscale Pyrolysis

Four different cylindrical reactors were constructed for the analysis: 1"x6" (diameter-length), 1.25"x8", 1.25"x12", and 3"x10". These reactors sizes were chosen to house the powdered and core samples with minimal dead volume. All reactors were constructed of 316 stainless steel rated to 4000 psi at 600°C. A ceramic heater band heated the 3" reactor and heating tape heated the smaller reactors. The reactors and fittings were insulated using glass wool and high-temperature silicon tape. High pressure Swagelok fittings were used for the 1"x6" and 1.25"x12" (diameter-length) reactors. These reactors were used to test the powder core samples (Sample #1 and Sample #2) and the 0.75" core (Sample #2), respectively. Graphite flanges were used to seal both ends of the 1.25"x8" and 3"x10" reactors. The flange reactors were used to test the 1" core (Sample #2) and 2.5" core (Sample #2), respectively.

Type K thermocouples were used to find the temperature profile through the core for each case. The thermocouples were inserted 0.6" into the core through 0.128"-diameter holes drilled through the reactor and the core sample as illustrated below in Figure 1. The 1.25" flange reactor had holes designed to monitor the temperature at the

center of the core (TC-1), the surface of the core (TC-4), and the surface of the reactor (TC-5). The two Swagelok reactors were designed to monitor TC-1 and TC-5. The 3" flange reactor was designed to monitor all five of the thermocouples in Figure 1.

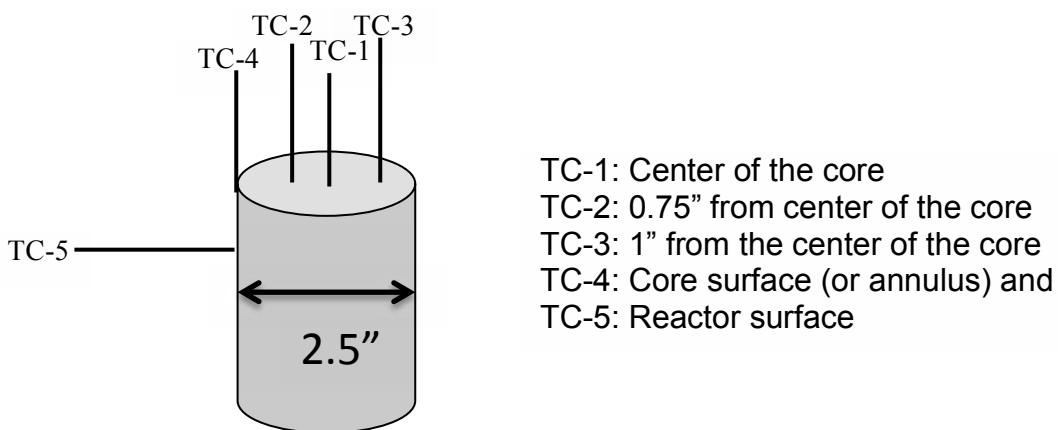


Figure 1. Schematic of thermocouple placement for the 2.5" core sample. All thermocouples used in the tests were type K.

The multiscale pyrolysis experiments were run in batch, semibatch, and continuous flow conditions at 350°C, 425°C, and 500°C and 0 or 500 psig. A specified heating rate was applied until the desired temperature was reached and then the sample was held at that temperature for 6, 12, or 18 hours. In batch mode, the system was closed and no products escaped the reaction chamber. This condition simulates an in situ condition where the formed products do not reach a pressure that fractures the rock. In semibatch mode, the system allows products to escape out of the top of the reactor with no sweep gas. This condition simulates a system where products escape only by their generated pressure and the given conditions. In continuous mode, the reactor is swept with gas so any product that is exuded is swept out of the reaction chamber and the secondary reactions are quenched. This mode simulates ideal conditions of high flow.

A schematic for the continuous flow experiments is shown in Figure 2. The system allowed for immediate collection of the products formed from the pyrolysis reaction. The products were then condensed, sampled, and analyzed. The walls of the chamber were heated and the reactor temperature was controlled using SPECVIEW

with either TC-1 or TC-5 depending on whether the experiment was isothermal or non-isothermal. The N_2 was preheated before entering the reaction chamber. Temperature and gas flow rates measurements were recorded using LabVIEW. Pressure was controlled using a Swagelok back pressure regulator (BPR). A heater kept the line from the reactor to the BPR at a constant temperature of 200°C. The condensers were cooled using a Brookfield TC501 bath with controller. Samples were taken using a 12-port autosampler with a VCOM interface.

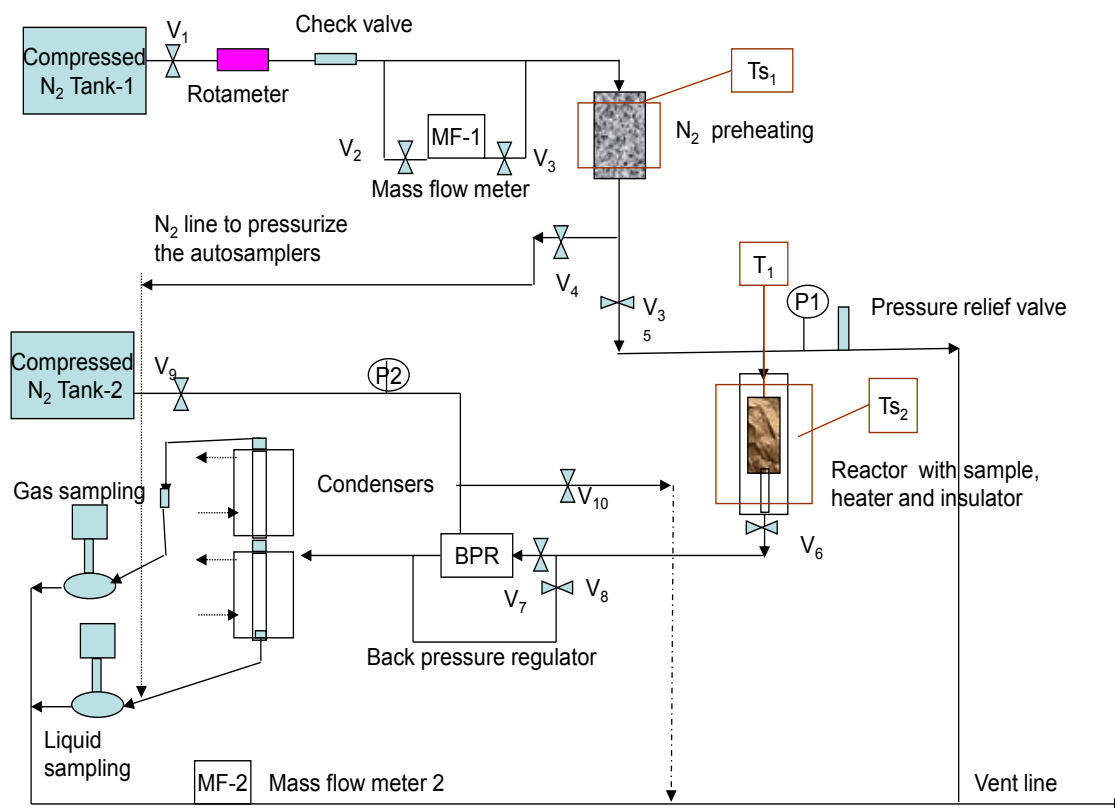


Figure 2. Experimental setup used to study the effect of operational parameters on yield and quality of the pyrolysis product distribution.

The bulk fluid was analyzed using GC and GC-MS. Spent shale was analyzed using a TGA differential scanning calorimetric instrument to estimate the amount of unreacted organic material and coke/char. Produced oil was analyzed using FTIR, densitometry, and rheometry.

4. Results and Discussion

Results of the TGA and multiscale pyrolysis experiments are presented below. Results for the HPTGA and TGA-MS experiments are not presented in this report. For full results and details, please see Tiwari [5]. The results included here affirm the models' validity in describing the phenomena that are occurring during oil shale pyrolysis.

4.1 TGA Results

Isothermal TGA results are not presented in this paper because they were not used in the kinetic model. Results from the nonisothermal TGA analysis of Sample #1 and the portion of Sample #2 that was powdered can be seen in

Figure 3. From the nonisothermal TGA data of Sample #1, kinetic parameters were calculated from the advanced isoconversional method described in a previous publication [7]. Fitted equations for the kinetic model can be found in Appendix: A. The fit of the model to the Sample #1 experimental data of normalized conversion (initial and final conversion set to zero and one, respectively) versus temperature is shown below in Figure 4.

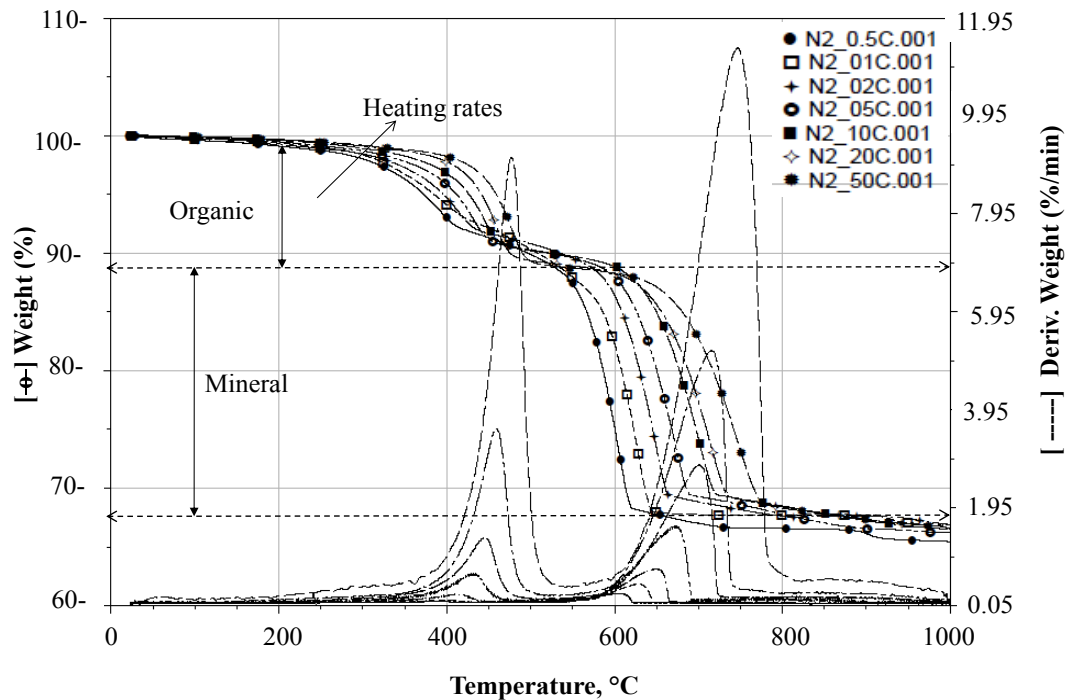


Figure 3. Nonisothermal TGA pyrolysis thermograms of Sample #1 at heating rates from 0.5°C/min to 50°C/min in an N₂ environment. The solid lines are weight curves and the dashed lines are corresponding derivatives. The first derivative peak represents organic weight loss and the second peak represents mineral weight loss.

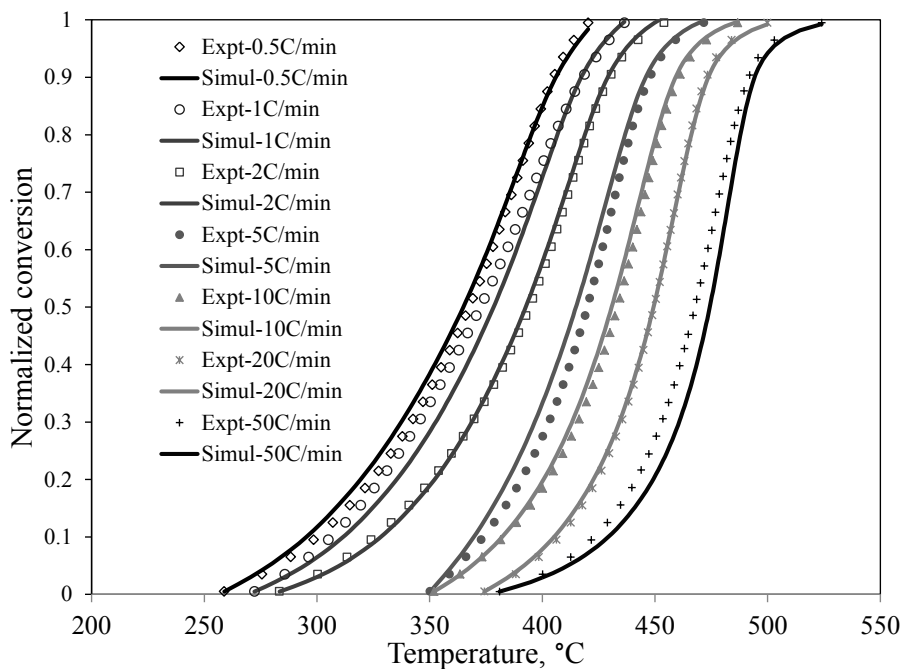


Figure 4. Experimental and simulated conversion profiles at different heating rates using the advanced isoconversional method.

4.2 Multiscale Pyrolysis Results

Pyrolysis was performed on four scales (powder and 0.75"-, 1"-, and 2.5"- diameter cores) using the apparatus shown in Figure 2. The results and findings are presented in this section.

Pyrolysis of Powder

Sample #1 was pyrolyzed in the 1" Swagelok reactor in batch, semibatch, and continuous flow conditions at 350°C, 425°C, and 500°C and 0 psig (ambient pressure) or 500 psig. Batch and semibatch conditions are more representative of an in situ process than a continuous flow condition with product removal. Immediate removal and quenching of pyrolysis products from the heated zone is impractical at an industrial in situ scale.

Results for batch experiments can be seen in Figure 5. The only significant coke (1.20%) in the batch experiments was formed after 18 hours of heating at 500°C and 500 psig. There was negligible coke formation at ambient pressure and 500°C. For the experiments at 350°C and 425°C and ambient pressure, the amount of unreacted organic content left in the rock was higher than the observed weight loss after 18 hours of reactor surface heating. Increased initial pressure led to increased weight loss at 6 and 18 hours.

The results for the TGA experiments run in semibatch mode can be seen in Figure 6. The opposite trend of temperature to coke formation was observed. The coke formation was all less than 1%, but for the 350°C semibatch experiment, approximately 0.80% of the sample was coke after 6 hours of TGA.

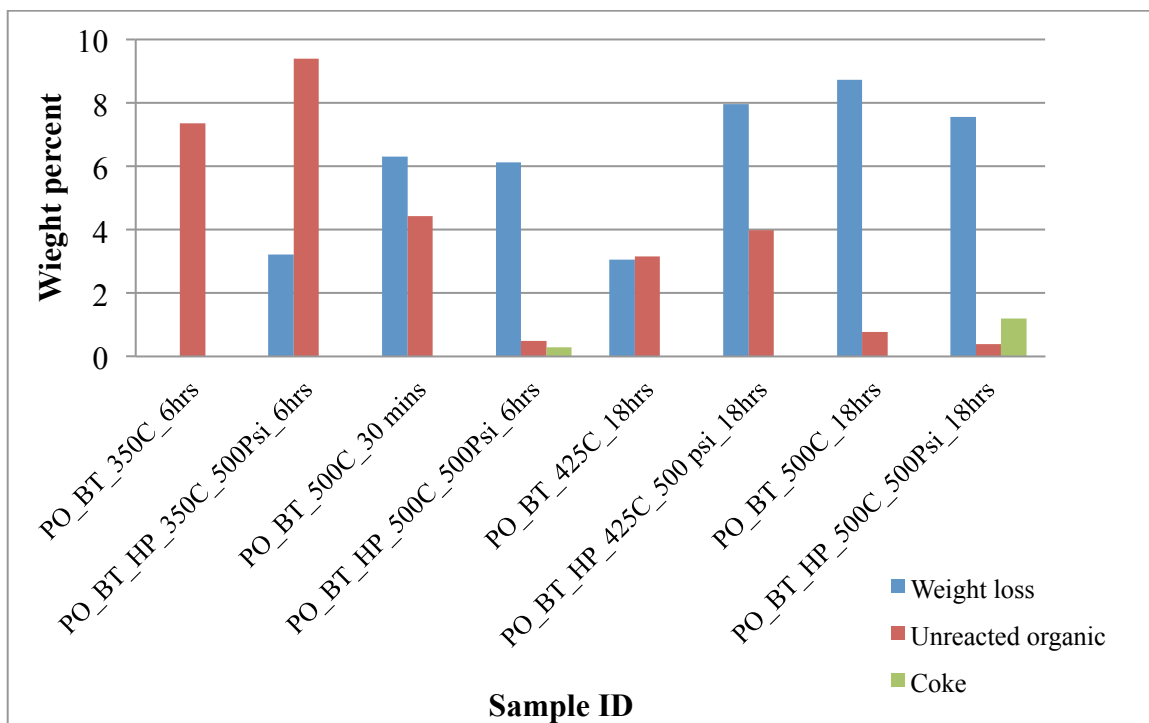


Figure 5. Weight loss, unreacted organic content, and coke results from Sample #1 batch pyrolysis are shown. Sample IDs are powder oil shale (PO), batch (BT), high pressure (HP) in psig, temperature in °C, and time in hrs.

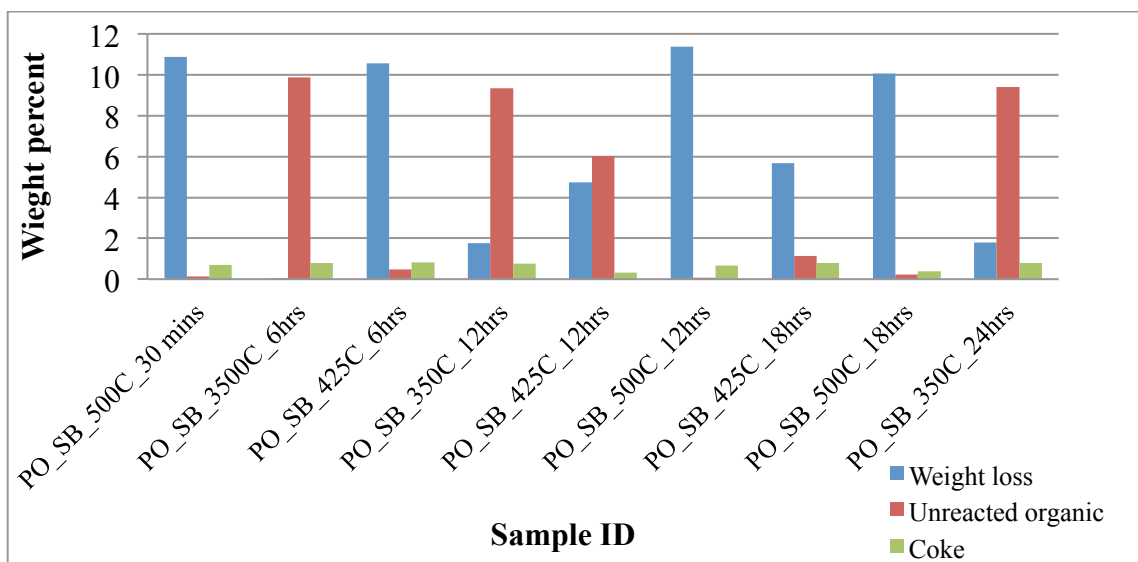


Figure 6. Weight loss, unreacted organic content, and coke results for semibatch TGA for Sample #1 are shown. Sample IDs are shown with powder oil shale (PO), semibatch (SB), temperature in °C, and time in hrs.

The results from batch and semibatch pyrolysis of Sample #1 show that the product composition is dependent on temperature, pressure, and residence time. This result is discouraging for proponents of in situ retorting because increased temperature, pressure, and process time creates more coke. Expending energy to create coke is not a favorable option.

Under continuous flow conditions no coke was found for heating rates below 5°C/min, but the coke yield in samples heated to 500°C at a rate of 10°C/min was 0.89%. The oil yield reflected the heating rate, i.e., higher heating rates yielded more oil.

The powder oil shale experiments provide insight into the balance between coke production and oil yield. An optimum exists in heating rates and extraction of oil. The best approach would be instantaneous pyrolysis followed by instantaneous product extraction and quenching, but for in situ processes, this approach is impossible.

Pyrolysis of 0.75"-Diameter Core

Table 4 lists the elemental analysis (CHNSO) of three 0.75"-diameter oil shale core samples after pyrolysis (spent shale) and of the pyrolysis products at three temperatures (300°C, 350°C, and 400°C). For comparison, the analysis of the powdered (raw) oil shale sample prior to pyrolysis is also included.

Table 4. Elemental analysis of three-0.75" oil shale cores and their pyrolysis products at three temperatures (300°C, 350°C, and 400°C). OS, SS, and SO denote raw oil shale, spent shale, and shale oil, respectively.

Samples	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)	Total	H/C (molar)	O/C (molar)
OS_Core	22.09	2.14	0.65	0.11	16.54	41.53	1.17	0.56
SS_CO_0.75"_300C	14.12	0.44	0.26	0.01	25.42	40.24	0.38	1.35
SS_CO_0.75"_350C	14.10	0.82	0.47	0.02	20.87	36.28	0.70	1.11
SS_CO_0.75"_400C	13.06	0.21	0.27	0.01	27.99	41.54	0.19	1.61
SO_CO_0.75"_300C	79.72	10.72	2.34	0.65	2.36	95.79	1.61	0.02
SO_CO_0.75"_350C	79.91	10.91	2.34	0.62	1.93	95.71	1.64	0.02
SO_CO_0.75"_400C	80.89	11.10	2.05	0.65	2.13	96.82	1.65	0.02

Results from the pyrolysis of the 0.75" diameter core are shown in Table 5. The reactor's surface was held at the indicated temperature for 24 hours after being ramped up at 100°C/min. For the ambient pressure experiments, the test at 400°C had the

highest oil yield and weight loss at ambient pressure. For the high pressure experiments (500 psig), the test at 500°C had the highest oil yield and weight loss. It can be inferred from Table 5 that the higher pressure results in a higher gas yield but does not change the oil yield much. Coke formation continues to be difficult to predict. It appears that the coke has an optimum for formation near 400°C and ambient pressure. As temperature and pressure change, equilibrium shifts the reaction away from coke formation.

Table 5. Results of 0.75" core isothermal reactor pyrolysis. OS is the original mass of the sample. Unreacted organics (UO) and coke values were found using TGA-DSC.

Sample-ID	Pyrolysis Conditions			Reactor Pyrolysis			TGA-DSC of SS	
	Temp (°C)	Press (psig)	OS (g)	Wt loss %	Oil Yield %	Gas Yield %	UO %	Coke %
CO_0.75"_Iso_500C_Ambient	500	0	47.71	15.30	10.71	4.59	0.08	0.33
CO_0.75"_Iso_400C_Ambient	400	0	41.39	16.77	12.46	4.31	2.66	5.78
CO_0.75"_Iso_300C_Ambient	300	0	50.88	1.08	0.64	0.44	15.52	1.16
CO_0.75"_Iso_500C_500psi	500	500	38.5	18.70	10.63	8.07	0.16	1.03
CO_0.75"_Iso_400C_500psi	400	500	39.09	9.67	2.06	7.61	7.68	0.22
CO_0.75"_Iso_300C_500psi	300	500	44.47	2.46	0.67	1.79	15.16	1.44

Pyrolysis of 1"-Diameter Core

Results from the pyrolysis of 1" core samples at 500°C and ambient pressure for three heating rates (1°C/min, 5°C/min, 10°C/min) can be seen in Table . Once the final temperature (500°C) was reached, the sample was held there for 2 hours. The results indicate that the lower heating rate yields more oil but at a cost of process time. The increase in oil yield may be due to the oil shale spending more time in a temperature range that limits secondary reactions such as coking and cracking, while the oil is expelled from the core. An advantage to the faster heating rate is a higher grade of oil produced (seen in Figure 7 and Figure 8).

Table 6. Results of 1" core nonisothermal pyrolysis at ambient pressure; heating rate (HR) and oil shale (OS) mass is measured in °C/min and g, respectively.

Sample ID	HR (°C/min)	OS (g)	Wt. Loss %	Oil Yield %	Oil Yield/Wt. Loss
CO_1"_1C/min_500C_Ambient_2hrs	1	145.08	15.34	8.76	0.57
CO_1"_5C/min_500C_Ambient_2hrs	5	144.46	13.50	8.20	0.60
CO_1"_10C/min_500C_Ambient_2hrs	10	145.32	10.41	7.66	0.73

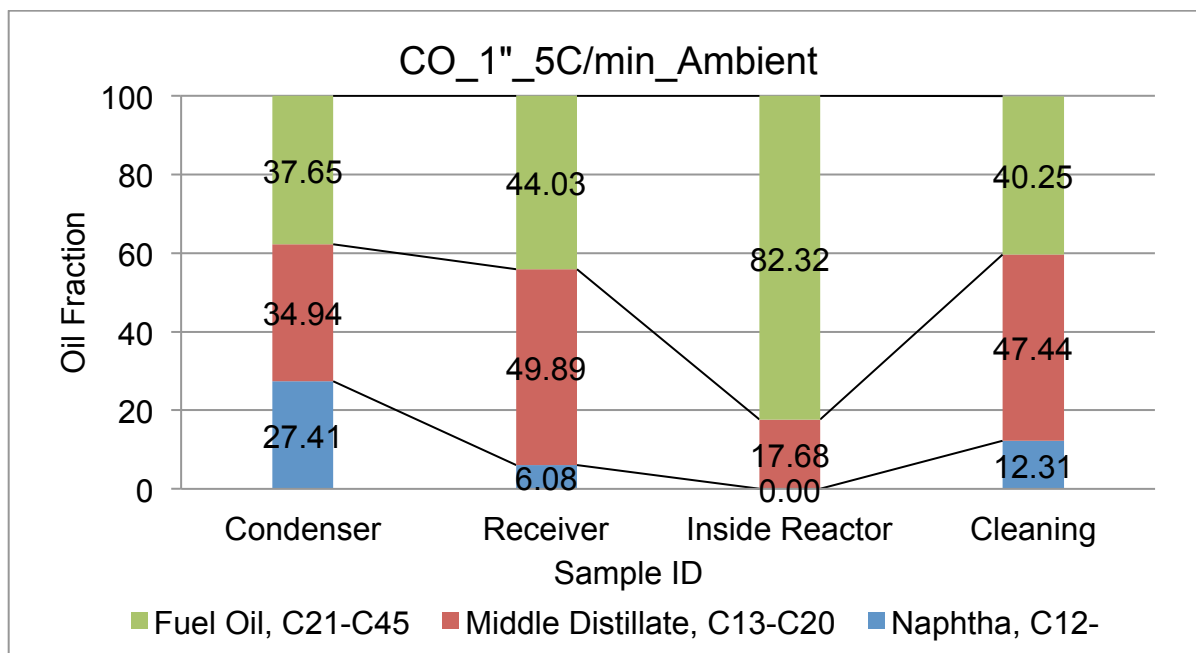


Figure 7. Grade of oil samples collected during the pyrolysis of 1" core (Sample #2) at a heating rate of 5°C/min to final temperature of 500°C.

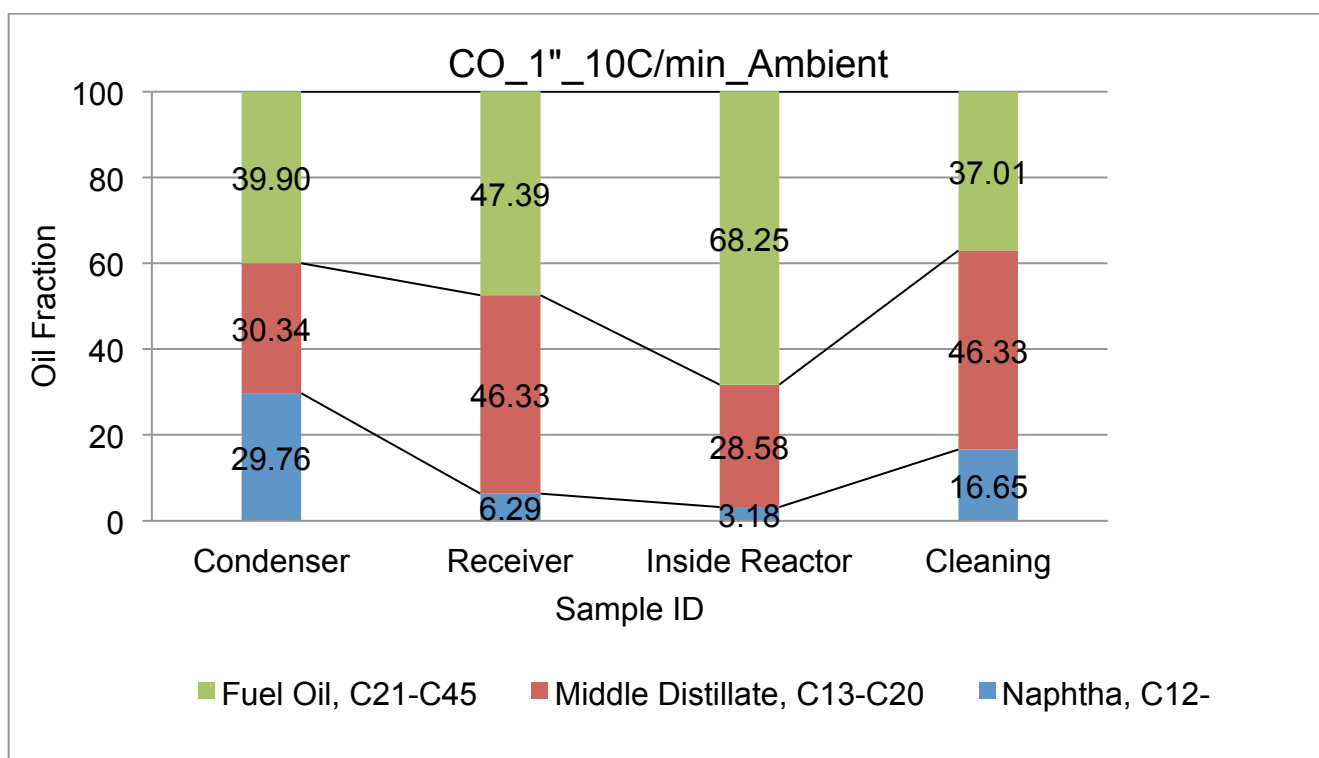


Figure 8. Grade of oil samples collected during the pyrolysis of 1" core (Sample #2) at heating rate of 10°C/min to final temperature of 500°C.

Pyrolysis of 2.5"-Diameter Core

The 2.5"-diameter core sample had the greatest heat and mass transport effects of the sizes tested, as expected. Results from isothermal experiments at 350°C and 500°C can be seen below in Table 6. The low weight loss in the 350°C and ambient pressure experiment can be attributed to the large temperature gradient (as seen in Figure 9). Pyrolysis begins when the oil shale reaches approximately 300°C [6]; only about 36% of the core will produce oil based on data shown in Figure 9. In the 350°C and 500 psig experiment, each thermocouple measured a temperature above 300 °C. The heat effects are not as prominent in the 500 psig experiments. This may be due to better heat transfer in the annular space and thus the surface of the core is kept at a higher temperature. With higher core temperatures in the pressurized experiments, there was a higher weight loss than the same experiments at ambient pressure. There was more gas produced at 500 psig than gas produced at ambient pressure as indicated by the oil yield/wt. loss% (see Table 6). The coke formed at high pressures and 500°C was 6.06% of the sample's original mass. The coke formation can be attributed to a longer residence time caused by a smaller pressure difference between the core and the reactor's annulus. Longer residence times at high temperatures increase secondary reactions (e.g., cracking and coking).

Table 6. Experimental results from 2.5" core (Sample #2, CO) pyrolysis at different isothermal reactor temperatures and different pressures.

Sample ID	Temp. (°C)	Pressure (psig)	OS, (g)	Wt. Loss (%)	Oil Yield (%)	Oil Yield/Wt loss
CO_2.5"_350C_Ambient_48hrs	350	0	493.58	3.67	2.77	0.75
CO_2.5"_350C_500psi_48hrs	350	500	695.15	14.44	8.32	0.57
CO_2.5"_500C_Ambient_48hrs	500	0	961.99	21.58	11.71	0.54
CO_2.5"_500C_500psi_24hrs	500	500	760.00	24.52	7.97	0.32

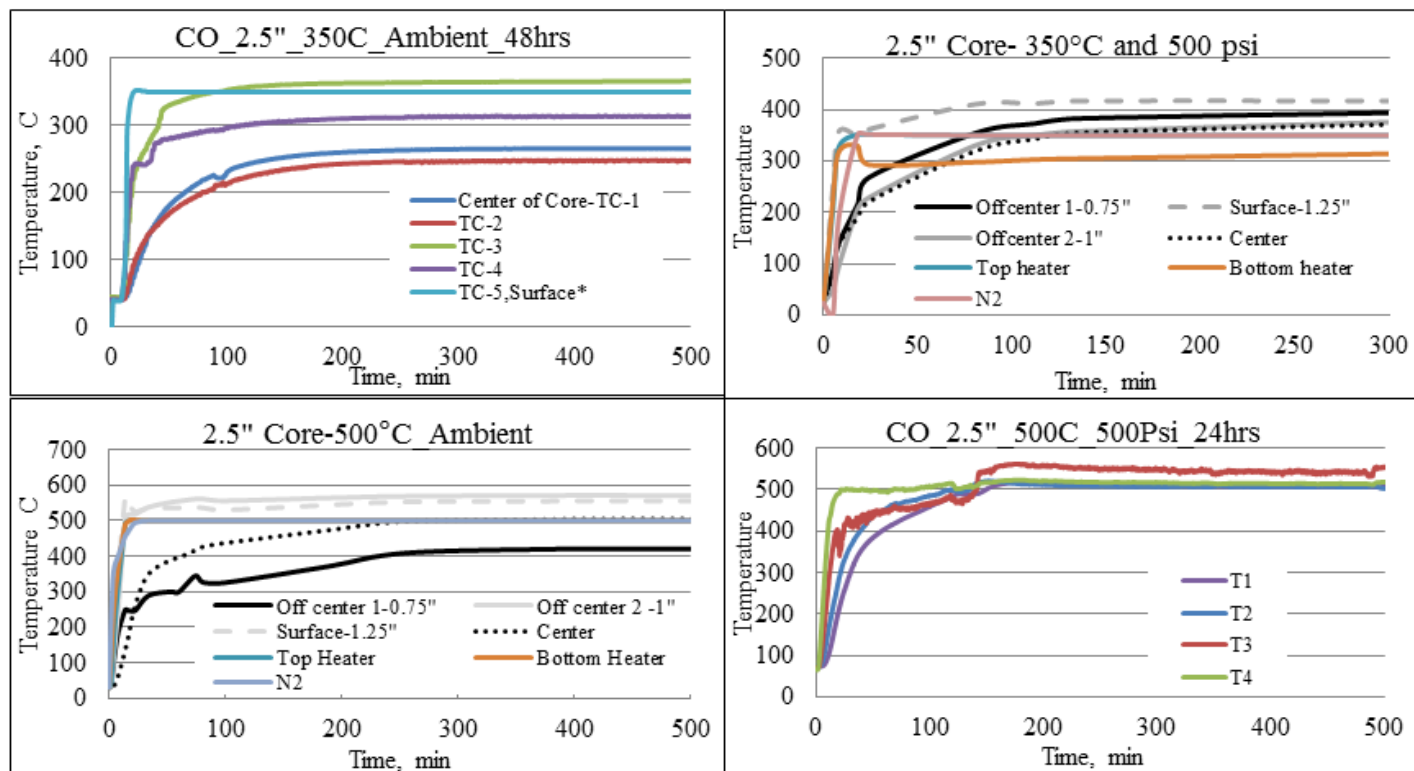


Figure 9. Temperature profiles during pyrolysis of 2.5" core sample.

The temperature distributions of the 2.5"-diameter core experiments are shown in Figure 9, above. The experiment with an isothermal surface temperature of 350°C and ambient pressure has a steady state temperature gradient of approximately 80°C/in. Heat transport effects are a limiting phenomenon for maturing kerogen in bulk quantities, such as those found in situ. There are anomalies in the temperature readings, such as the in 2.5"-diameter core at 500°C and ambient pressure experiment where the off center 2 -1" reading was higher than the surface temperature. These anomalies are most likely from the heterogeneity of the core, deviance from ideal conditions (e.g., symmetry, insulation, etc.), and/or secondary reactions.

Size Comparisons

A comparison of the 2.5"- and 0.75"-diameter core experiments at 500 psig is shown in

Table 7. Because the larger core has a longer residence time for the oil, the oil

undergoes secondary reactions of coking and cracking which decreases oil yield while increasing gas and coke. In the larger core, the weight loss is higher which could be beneficial in increasing the flow pathways for the products.

Table 7. Comparison of overall mass balance of 2.5"-diameter and 0.75"-diameter core isothermal reactor surface experiments at 500°C and 500 psig.

Material Balance	CO_2.5"_500C_500psi_24hrs	CO_0.75"_500C_500psi_24hrs
Wt. loss %	24.52 %	18.69 %
Oil yield %	7.96 %	10.63 %
Coke %	6.06 %	1.03 %
Gas %	16.56 %	8.06 %
Unreacted organics%	0.05 %	0.43 %

Conclusions that are drawn from the comparison of the results are that higher temperature experiments had higher weight losses but also increased the amount of coke formed. The grade and the yield of the oil were dependent on both final temperature and heating rate. Higher pressure increased the rate of coking and cracking reactions, yielding more coke and gas. Coking and cracking are dependent on the residence time of the oil in hot zones.

Larger core sizes have greater heat and mass transport resistance. As the heat moves into the core, the internal core pressure increases due to reactions and thermal expansion and the pressure pushes the products out of the sample. Expulsion of the products from the core is similar to a batch powdered-core pyrolysis experiment. The time-temperature history governs the product generation and expulsion. The oil shale's resistance to sudden temperature changes makes the isothermal heating regime more desirable than the nonisothermal heating regime. This effect was seen in comparing the 1" core experiments with a 5°C/min and a 10°C/min heating rate inside the reactor; more naphtha and middle distillate range oils were produced with the 10°C/min heating rate.

5. Modeling

A flowchart describing the oil shale pyrolysis model can be seen below in Figure 10. There are four physical processes included in the model: mass transfer, heat transfer, reaction kinetics, and thermodynamics. The model was developed using COMSOL Multiphysics simulation software. COMSOL can be used to solve systems of differential equations for fluid mechanics, thermodynamics, heat transfer, and reaction kinetics among other physical phenomena. Input parameters included properties of the oil shale and its products, operating conditions, and duration. The simulator uses all of the input parameters to populate the fields in the coupled model (see Appendix: A). Core temperature distributions, concentration profiles, and product yields were the outputs. The objective of the simulation was to test if the model's results were similar to those observed in the experiments.

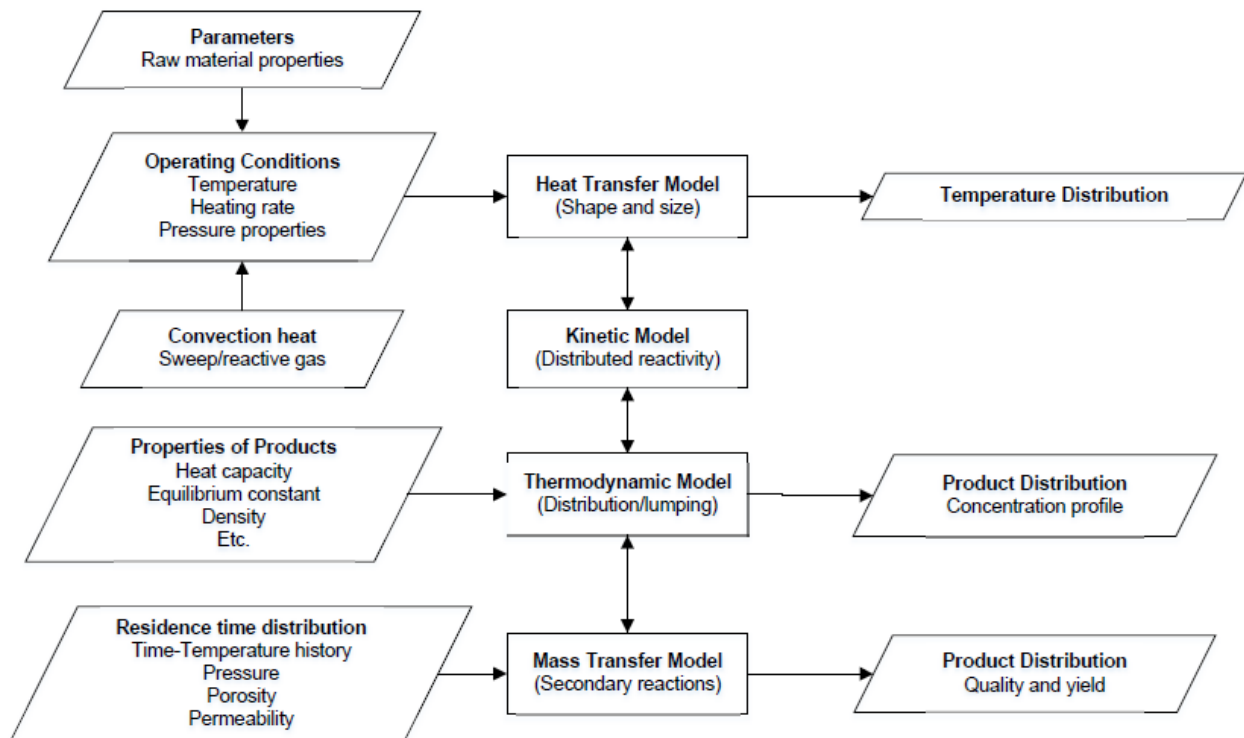


Figure 10. Flowchart for oil shale pyrolysis simulation.

A 2.5" diameter core sample with 18% organic material (kerogen) was simulated. The simulation assumed isothermal surface heating and reaction kinetics described in

Appendix: A. The assumed molecular weights of the kerogen and the pyrolysis products are given in the Table 8. Kerogen (CK) is the organic content in the oil shale. HOIL (HO) is the heavy oil produced in the TGA, which includes C₁₂ and up. LOIL (LO) is the condensable hydrocarbon fraction, C₄ to C₁₁, and GAS includes all noncondensable hydrocarbons at -6°C and ambient pressure. Each of these compounds was simulated in the overall reaction. No mineral reactions were taken into account.

Table 8. Elemental model (C and H) and molecular weight of kerogen and pyrolysis products.

Compound	C	H	Ratio (H/C)	Molecular Weight
Kerogen	1479.000	2220.000	1.501	20000.550
Heavy oil	31.751	42.818	1.349	424.492
Light oil	11.189	17.510	1.565	152.034
Gas	3.354	11.634	3.468	52.011
Methane	1.000	4.000	4.000	16.042
Coke	1.185	0.316	0.267	14.552
Char	1.004	0.546	0.544	12.604

The simulation was done in two dimensions to simplify the computation (see Figure 11). Boundary conditions were fixed at 400°C and open to flow. Initial conditions included a temperature of 27°C in the core and no products. As the core was heated, reaction kinetics determined when particular reactions started and to what extent they progressed.

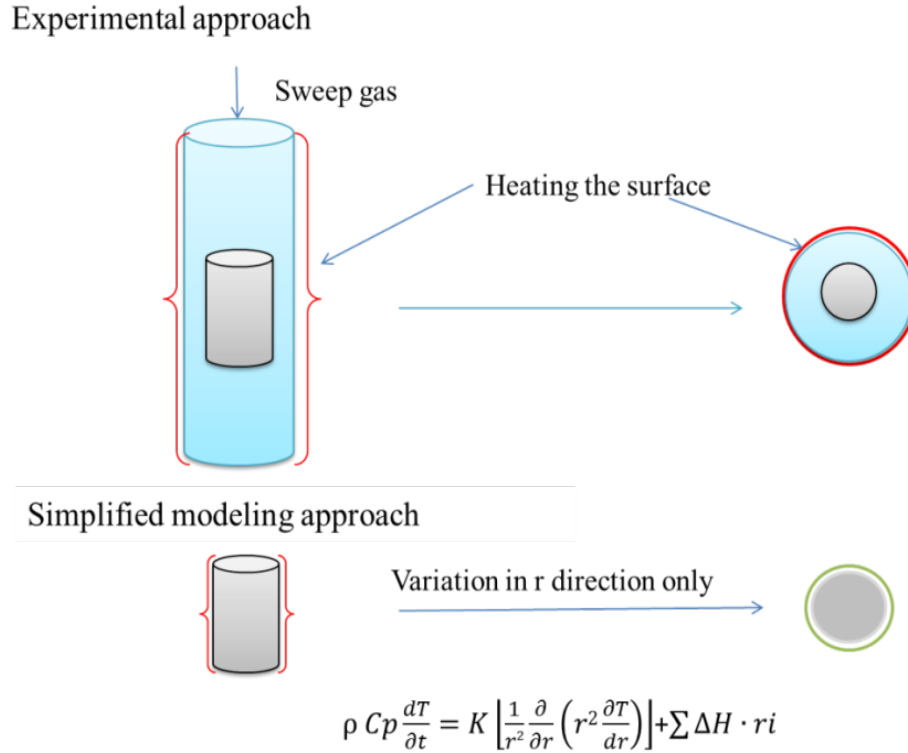


Figure 11. Simplified geometric model from reactor to COMSOL simulator.

The simulation and experimental temperature profiles are similar but have different steady state temperatures. Theoretically, the temperature of each indicator should come to the temperature of the isothermal surface. However, there was a heat sink within the experiments that was not accounted for in the model. The presence of the heat sink created discrepancies between the experimental data and the simulation. Modeling the heat sink created data that was similar to the experiment, but further investigation is needed.

The simulated results for the mass fractions are similar to the experimental results with an oil yields of 11% (as seen in Figure 12) and 12% oil yield (as seen in Table 6) respectively. Comparing the two sets of results from the 2.5" core isothermal 400°C surface heating simulation and the analogous multiscale experiment, CO_2.5" _500C _Ambient _48hrs, 12% weight loss in the simulation (OIL+GAS) is much less than the 21.58% weight loss seen in the multiscale experiment. The maximum weight loss the simulation could have was 18%. The difference between the simulation

and experiment is from low temperature mineral reactions or heterogeneity. Sample #2 was tested to have an average of 17.5% organic material in the TGA but had a weight loss above 20% for the multiscale experiments.

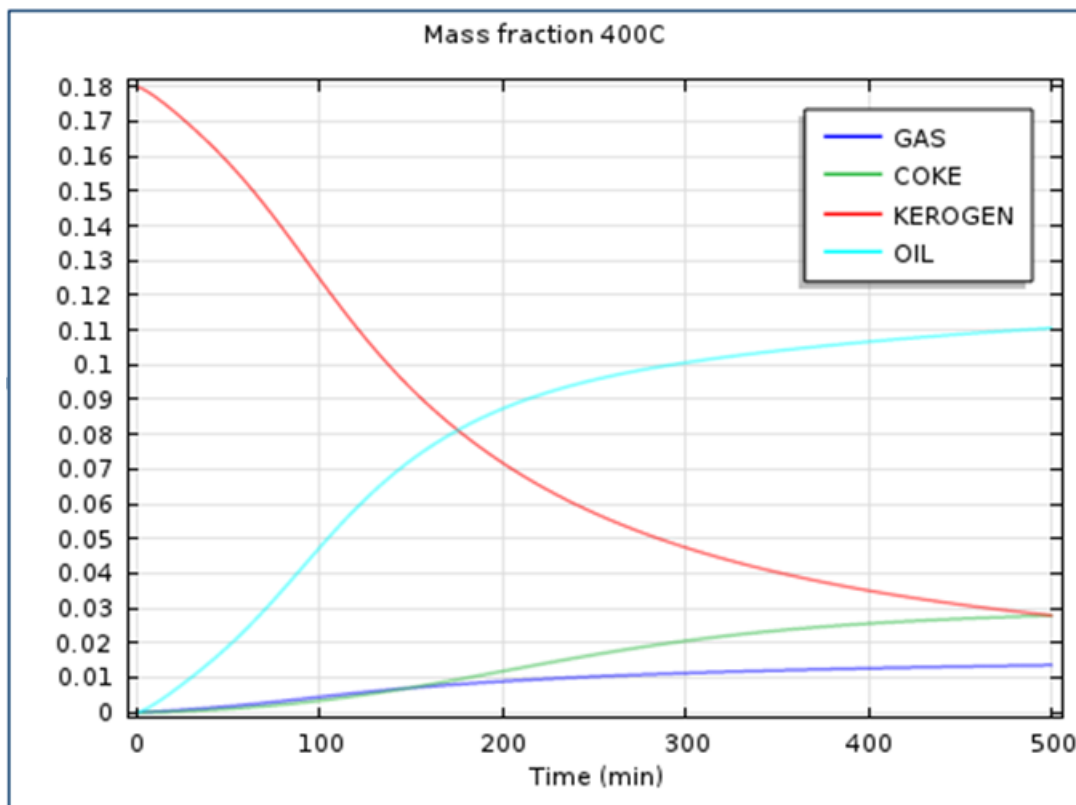


Figure 12. Mass fractions versus time at a constant surface temperature of 400°C.

Secondary reactions of cracking and coking are an important part of the model because cracking and coking reduce the oil yield. Without the secondary reactions in the model, the simulation produces higher oil yields than what are seen in the experiments. Heat propagation through the core initiates the pyrolysis followed by cracking and coking; products are constrained by an elemental mass balance. The simulation confirms the experimental finding that the in situ process must have channels of flow to reduce gas and coke formation.

The physics used in the simulation affect the conversion and product distribution. The model is basic and has some assumptions that reduce its accuracy. Other physical phenomena such as multicomponent thermodynamics, multiphase flow,

multicomponent heat transfer, more extensive reaction sets, etc., would improve the predictive quality of the model.

6. Conclusions

The TGA and multiscale pyrolysis experiments were used to study the effects of core size, heating regime, pressure, and final temperature on product distribution and oil yield. It was found that larger core sizes produced more coke and gas per unit mass of core sample. This result indicated that secondary reactions were occurring inside the core sample. It was found (1) that the effectiveness of a nonisothermal heating regime was dampened by heat transport effects in core sizes larger than 1"-diameter, (2) that higher pressure lowered the temperature gradient in larger core samples, and (3) that the greatest oil yield occurred in the 400°C isothermal surface heating experiment. Therefore, isothermal heaters would be recommended. More research is required to determine if a higher temperatures and cracking could create enough back pressure to move products through the rock to a collecting well. The findings presented here provided a model to optimize time, energy, product distribution, and oil yield.

Upscaling from bench scale to pilot scale requires a model that is robust enough to account for the pressure, temperature, and volumetric effects that would occur in situ. A pilot scale in situ experiment needs to be coupled a model that captures more of the physics of in situ heating production before simulation results with quantified uncertainty can be provided. Pilot scale validation is needed to quantify potential macro channels that may be created from oil shale pyrolysis. Larger core samples may be an alternative to a pilot scale in situ pyrolysis. Larger core samples will provide researchers with the ability to observe how the oil shale rock will crack and fracture due to the thermal expansion, kerogen degradation, oil/gas expansion, and pressure changes.

The research done in this paper and future research will provide a base for new technology to make oil shale a more viable source of long-term energy. Fundamental characterization of Green River oil shale along with models that describe how oil forms and moves during pyrolysis is a step towards the technology that will make oil shale pyrolysis economic and environmentally sustainable.

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Appendix: A

Equations

Kinetics:

$$R_i = -A \times e^{-\left(\frac{E}{RT}\right)} \times C_i$$

$$R_{CK} = k_1[CK] * \rho_{org}$$

$$R_{HO} = (0.7915 * k_1[CK] - k_2[HO]) * \rho_{org}$$

$$R_{LO} = (0.1054 * k_1[CK] + 0.7800 * k_2[HO] - k_3[LO]) * \rho_{org}$$

$$R_{GAS} = (0.06509 * k_1[CK] + 0.007201 * k_2[HO] + 0.0008216 * k_3[LO] - k_4[GAS] + 0.09299 * k_5[CHAR]) * \rho_{org}$$

$$R_{CHAR} = (0.02440 * k_1[CK] + 0.2118 * k_2[HO] + 0.6512 * k_3[LO] + 0.1243 * k_4[GAS] - k_5[CHAR]) * \rho_{org}$$

$$R_{METHANE} = (0.01368 * k_1[CK] + 0.0009800 * k_2[HO] + 0.3480 * k_3[LO] + 0.8755 * k_4[GAS] + 0.01235 * k_5[CHAR]) * \rho_{org}$$

$$R_{COKE} = 0.8948 * k_5[CHAR] * \rho_{org}$$

Where

$$k_1 = A_1 e^{-\left(\frac{E_1}{RT}\right)}$$

$$k_2 = 1.00 * 10^{13} e^{-\left(\frac{2.08 * 10^5}{RT}\right)}$$

$$k_3 = 5.00 * 10^{11} e^{-\left(\frac{2.33 * 10^5}{RT}\right)}$$

$$k_4 = 1.20 * 10^{12} e^{-\left(\frac{2.70 * 10^5}{RT}\right)}$$

$$k_5 = 1.38 * 10^{13} e^{-\left(\frac{2.26 * 10^5}{RT}\right)}$$

And

$$A_1[1/s] = e^{-3.48E4 * X^{10} + 1.51E5 * X^9 - 2.78E5 * X^8 + 2.85E5 * X^7 - 1.76E5 * X^6 + 6.78E4 * X^5 - 1.61E4 * X^4 + 2.35E3 * X^3 - 2.21E2 * X^2 + 50.3 * X + 9.78}$$

$$E_1[kJ/mol] = -2.48E5 * X^{10} + 1.09E6 * X^9 - 2.06E6 * X^8 + 2.15E6 * X^7 - 1.36E6 * X^6 + 5.39E5 * X^5 - 1.32E5 * X^4 + 1.98E4 * X^3 - 1.79E3 * X^2 + 3.06E2 * X + 91.4$$

Heat transfer:

$$\rho \cdot C_p \frac{\partial T}{\partial t} + \nabla(-k \nabla T) = Q - \rho \cdot C_p \cdot \vec{u} \nabla T$$

Where

$$\rho = \frac{\rho_{organic} \cdot \rho_{rock}}{\frac{m_{org}}{m_{total}} \times (\rho_{rock} - \rho_{organic}) + \rho_{organic}}$$

$$C_p = 4186.8383 \times (0.172 + (0.067 + 0.00162 \times Grade_{oil\ shale} \times C_{oil}) \times (10^{-3} \times 1.8 \times T))$$

$$K = 1.73074 \times (a_1 \times (1 - b_1 \times (1.8 \times (T - 273.15) - 53) - b_2 \times (1.8 \times (T - 273.15) - 53)^2) \times \exp(a_2 \times Grade_{oil\ shale} * C_{oil}))$$

$$Q \left[\frac{W}{m^3} \right] = -DH = -370 \left[\frac{kJ}{kg} \right] * k_1[CK] \rho_{org}$$

Mass transfer:

$$u = \frac{K_p}{\mu} \nabla p$$

$$K_p = \frac{D_p^2 \times \varepsilon^3}{150 \times (1 - \varepsilon)^2}$$

$$\frac{\partial}{\partial t}(\rho \varepsilon) + \nabla \cdot (\rho u) = Q_m$$

$$\varepsilon = 0.003 + (0.0146 + 0.0129 \times (Grade_{OS} \times X_{CK}) - 0.000046 \times (Grade_{OS} \times X_{CK})^2)$$

$$\rho = \frac{pM}{RT}$$

Thermodynamics:

Assumed fluid followed the ideal gas law

$$\rho = \frac{pM}{RT}$$

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