

**EXPERIMENTAL STUDY OF IN SITU COMBUSTION WITH TETRALIN AND
METALLIC CATALYSTS**

A Thesis

by

EMUOBONUVIE PALMER-IKUKU

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2009

Major Subject: Petroleum Engineering

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Chair of Committee,
Committee Members,

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ABSTRACT

Experimental Study of In Situ Combustion with
Tetralin and Metallic Catalysts. (August 2009)

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Chair of Advisory Committee: Dr. Daulat D. Mamora

Experimental studies showed the feasibility of adding metallic catalysts and tetralin for the upgrade and increased recovery of heavy oil during the in situ combustion process. Further experimental studies also showed the applicability of in situ combustion as a viable method of upgrading and improving recovery of intermediate oils.

Three successful experimental runs were performed with heavy oil from Mexico (10.1°API gravity). The first run was the control run without the addition of tetralin or metallic catalysts; the second run used heavy oil premixed with 3 wt% tetralin and 500ppm nickel catalyst; and the third run was with heavy oil premixed with 3 wt% tetralin and 500ppm iron catalyst. For the three runs, the cell production pressure was kept constant at 300 psig. The combustion cell was placed in a vacuum jacket and set to a temperature of 60°C. For the only successful run with the intermediate Texas oil (22.0°API gravity), the production pressure was also kept constant at 300 psig but the vacuum jacket temperature was set to a reservoir temperature of 40°C. During the runs for both oils, samples of produced oils and combustion flue gases were collected at

regular intervals for analysis. These analyses included determination of oil viscosity and density, oil recovery, combustion front velocity, and apparent H/C ratio.

Experimental results for the intermediate oil run, the oil gravity increased by 6 points showing the upgrading effects of in situ combustion on intermediate oils. Also, the high average combustion temperatures observed during the run indicated that in situ combustion may be applicable to reservoirs of similar characteristics to the intermediate Texas oil reservoir.

Heavy oil experimental run results indicated that the use of tetralin and metallic catalysts increase the average combustion front temperature from 484°C to 501°C for the run with nickel catalysts, and from 484°C to 492°C for the run with iron catalysts. These results also show an increase in produced oil recovery from 83% to 90% of oil initially in place for the nickel catalyst run, and 83% to 86% of oil initially in place for the iron catalyst run.

DEDICATION

I would like to give my most sincere gratitude to God for his faithfulness and steadfast guidance through my time at Texas A&M University in the Department of Petroleum Engineering.

ACKNOWLEDGEMENTS

I would like to express heartfelt gratitude to my committee chair, Dr. Daulat. M. Mamora, for his unflinching support and advice through my two years at Texas A&M University in the Department of Petroleum Engineering. For this support, I am most grateful. I would also like to thank my committee members, Dr. J. Schubert and Dr. Y. Sun, for their relentless encouragement and academic support.

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1 INTRODUCTION

Crude oils are conventionally classified into three groups based on specific gravity. Heavy oils, API gravity range of 10° to 20°; intermediate oils, API gravity range of 21° to 30°; and light oils, API gravity greater than 30°. ¹

With increasing demand for oil as a result of the high growth rate in most developing countries, there has been a steady shift of attention to unconventional petroleum resources. Heavy oils are usually termed unconventional petroleum resources because unconventional methods are required for its production to the surface.

Heavy oil reservoirs contain highly viscous crude that have very low mobility thus creating transportation and processing problems. To increase mobility in such reservoirs, the oil viscosity has to be reduced. Thermal recovery methods such as steam flooding, Steam Assisted Gravity Drainage (SAGD), cyclic steam injection and in situ combustion are some of the enhanced recovery methods currently been used to reduce heavy oil viscosity and therefore improve oil recovery. These methods basically use heat which is injected or generated in situ as the principal mechanism to reduce the oil viscosity. The major difference between steam flooding process and in situ combustion is that unlike in the former where steam is injected, steam is produced by vaporizing water already in the rock formation with heat from the in situ combustion of some of the oil in the reservoir.

In situ combustion is one of the oldest methods of thermal recovery. It was originally conceived to improve recovery of oil from highly viscous oil reservoirs. The process maybe used not only to improve recovery in heavy oil reservoirs but also for intermediate and light oil reservoirs.

The advantages of in situ combustion over steam injection methods include:

1. Steam injection may not be suitable for deep reservoirs (greater than about 3,000ft) because wellbore heat losses at this depth would be very high. To ensure improved recovery by oil viscosity reduction, steam injected must be at steam temperature or reach steam temperature in a short period of time at the bottom of the injector.
2. Heat losses to adjacent layers in thin reservoirs also make steam injection less suitable. There have been economically successful projects implemented in reservoirs ranging in thickness from 4-150ft.
3. Total environmental impact is less for in situ combustion when compared with other thermal recovery methods because the combustion takes place in the reservoir.
4. In situ combustion projects permit the use of wider well spacing and can result in higher oil recovery in comparison with steam injection.

The disadvantages of in situ combustion over steam injection methods include:

1. Safety issues that can be magnified by the higher temperatures and/or chemical reactions taking place in the injectors and producers.
2. Corrosion can also be a problem when the injected gas has not been properly dehydrated. Also, flue gas with high sulfur content can create corrosion problems
3. Sweep efficiency of the in situ combustion process is low as the movement of the combustion front cannot be controlled.
4. Air compressor reliability has to be guaranteed throughout an in situ combustion operation as failure of a compressor would make the combustion front die.

5. The planning and design stage for the in situ combustion project is more expensive. The design of this process is often preceded by experimental studies that determine the fuel availability, air requirements and the burning characteristics of the oil.
6. Problems of channeling, because of unfavorable rock heterogeneities (Mamora, 1993).

The most common kind of in situ combustion is the dry forward combustion process. In this process, air is injected into an injection well, for a short time and then the oil in the formation is ignited. Ignition is usually induced using down-hole gas burners, electric heaters or through injection of a pyrophoric agent (such as linseed oil) or a hot fluid such as steam. The heat generated at the combustion front propagates, by conduction and convection, through the reservoir towards the production well. Martin et al. (1958) and Ramey (1971) showed that the convective heat wave velocity for the case of air injection is about one-quarter that of the combustion front. As the front progresses, several well characterized zones are developed in the reservoir between the injector and the producer. The locations of the various zones in relation to the injector and the producer are shown below in Fig. 1.1.

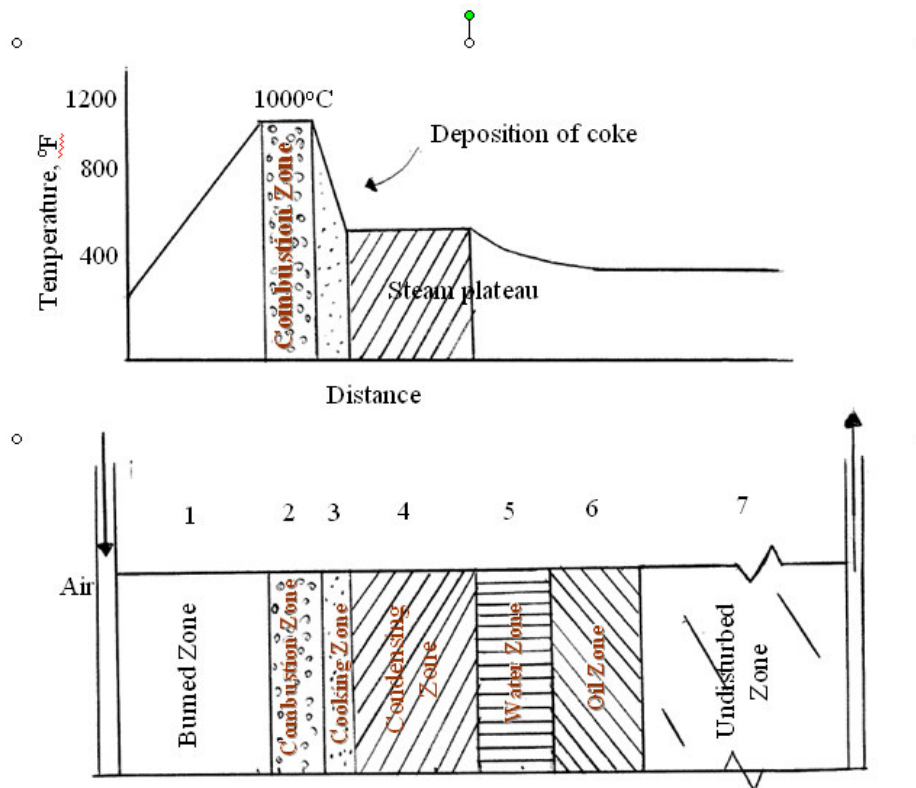


Fig. 1.1—In situ combustion schematic temperature profile.

Another kind of in situ combustion is the wet combustion method. In this process, water and air are injected simultaneously or alternately. Water is injected to absorb and transport heat many more times efficiently as compared to air. Injection of air simultaneously or alternately with water is commonly known as wet, partially quenched combustion. The ratio of the injected water to the air rate influences the rate of burning front advance and the oil displacement behavior. This method may be considered for thin reservoirs where heat loss to adjacent formation is significant. The injected water absorbs heat from the burned zone, vaporizes into steam, passes through the combustion front, and releases the heat as it condenses into the cooler sections of the reservoir. Thus, the growth of the steam and water banks ahead of the burning front is accelerated, leading to more efficient oil displacement.

Another form of in situ combustion is the reverse combustion process. In this method, the combustion zone is initiated at the producer as the nomenclature suggests. The reverse combustion front travels countercurrent to the air towards the injection well where air is injected. The basic concept in this process is that most part of the heat generated remains between the production well and the oil when it is mobilized. So, when the oil begins to move, insignificant cooling occurs to stop the oil from moving towards the producer.

Viscosity reduction during in situ combustion can be achieved either by a thermal hydro-cracking process or by hydro-cracking process with supported agents such as catalysts, caustic or by a preceding process such as solvent injection. Thermal hydro-cracking without catalysts has shown a significant increase of API gravity of the heavy

oil produced, including an undesirable high coke formation (25%) while hydro-cracking supported with catalysts not only increased API gravity but also improved the quality of produced oil (Sarathi *et al.* 1998).

During combustion, the addition of tetralin and metallic catalysts can help improve the in-situ combustion process. The catalysts increase the molar CO₂/CO ratio values of fuel combustion while tetralin acts as a hydrogen donor. These catalysts also decrease the atomic H/C ratio with an increase in temperature and increase the reaction order, m , in the Arrhenius equation as the concentration of the additives increase.

1.1 Research objectives

The overall objectives of the project were:

1. Evaluate experimentally the possibility of upgrading and improving recovery of a heavy oil (10.1°API) from Mexico by in situ combustion using tetralin and ionic based metallic catalysts. For this research, we conducted experiments using nickel, and iron catalysts in conjunction with tetralin. The results were compared to control experiments utilizing no tetralin or catalysts.
2. Determine the applicability of in situ combustion to a Texas intermediate oil (22.0°API) while also evaluating the upgrading effects of in situ combustion on intermediate oils.

To achieve these objectives, I conducted the following experiments:

1. One base run (original heavy oil from Mexico, 10.1°API)
2. A run with a mixture of heavy oil, tetralin and ionic based nickel solution (500ppm)

3. A run with a mixture of heavy oil, tetralin and ionic based iron solution (500ppm)
4. A run with a Texas oil (22.0°API)

The extent of upgrading was established through various analyses of the produced and initial crude oil. For the heavy oil runs, the following measurements for the runs with tetralin and catalysts were compared with that of the original oil run.

1. Composition of flue gas from combustion
2. Apparent H-C ratio (F_{HC}), m -ratio and the air-fuel ratio (F_{AF})
3. Average combustion temperatures.
4. Combustion front velocity
5. Cumulative volume of produced oil and the recovery factors
6. Produced oil density and produced oil viscosity at different times and temperatures.

These measurements helped determine the effectiveness of tetralin and the catalysts on in situ oil upgrading.

To determine if the Texas oil will sustain in situ combustion, I analyzed the air – fuel ratios and the temperature profile during the run. Also, the produced oil density and produced oil viscosity were compared to the oil viscosity and oil density of the original oil before the in situ combustion process to evaluate the upgrading effects of in situ combustion.

2 LITERATURE REVIEW

Numerous studies have been conducted to improve the in situ combustion process. Solvent injection followed by combustion, addition of caustic to the combustion process, and addition of metallic additives are some of the methods that have been investigated in the past. For this research, we investigated the use of tetralin in conjunction with different metallic catalysts for in-situ oil upgrading. We also conducted experiments to evaluate the applicability of in situ combustion to intermediate oils. In this section, a literature review of relevant previous studies is described.

Castanier *et al.* (1992) conducted thirteen combustion tube runs using four different crude oils to investigate the upgrading of heavy oil by in situ combustion with metallic additives. For all cases, transition metals such as tin, iron and zinc were used as additives to improve combustion efficiency. Results showed that the amount of fuel deposited increased in the order: zinc, original oil without additives, iron and tin for Huntington oil. For Hamaca crude, the fuel deposition increased in the order: original oil, iron and tin. From results obtained, it was evident that among the metallic additives used, iron and tin increased efficiency of the combustion, reducing the amount of oxygen produced and eliminating the fluctuations in gas compositions observed during the control runs.

Wichert *et al.* (1995) conducted a systematic study to investigate the effect on the low temperature oxidation of heavy oil during in situ combustion. This study was based on the inhibitive characteristics of caustic so it was expected that oxidation reactions will be inhibited. These experiments were conducted by varying caustic concentrations, temperatures, oxygen partial pressures, and run times. Results indicated that a decrease

in viscosity occurred at lower caustic concentrations. However, the presence of caustic did not inhibit the oxidation reactions from taking place, but rather impeded the conversion of asphaltenes to coke.

He *et al.* (2005) proposed a cationic exchange of metallic salts with clay as a mechanism to create activated sites that enhance combustion reactions between oil and oxygen. Combined tube runs were conducted to gauge combustion performance and measure the kinetics of combustion. Runs with metallic additives showed a remarkable improvement in the following characteristics including lower activation energy, greater energy consumption, lower temperature threshold, more complete oxidation and an increased oil recovery.

Cristofari *et al.* (2006) investigated experimentally the applicability of cyclic solvent injection into heavy crude oil followed by in situ combustion in the upgrading of heavy oil. Hamaca (Venezuela) and West Saks (Alaska) crude oils were used for these experiments. The work was based on the proven upgrading characteristics of the two processes. Pentane, decane and kerosene were used as solvents for the injection process. Different results were obtained for both oils. Hamaca oil exhibited good burning properties and an upgrade just after solvent injection while West Saks did not present stable combustion properties after solvent injection and combustion. Results from the experiments showed that solvent injection prior to combustion recovers most of the light oil fractions by extraction. These fractions could have been degraded by combustion. From the experiments, pentane showed better upgrading qualities when injected for oil that experienced less fuel deposition while decane and kerosene showed better upgrading

characteristics for oils with high fuel deposition. Most importantly, this study showed the applicability of this process to a broad range of reservoirs.

Nares *et al.* (2007) studied the effect of organo-metallic catalysts and a hydrogen donor on thermal hydro-cracking. The study showed the application of organo metallic catalysts with a hydrogen donor could improve the quality of crude oil therefore increasing productivity index. For the thermal hydro-cracking process without catalysts, crude oil was injected in a batch reactor and pressurized. For the hydro-cracking process with supported catalysts, heavy oil was pre-mixed with organo-metallic catalysts then injected in the batch reactor. The results from these studies served as precursors to the in situ combustion test runs conducted by Ramirez *et al.* (2007).

Ramirez *et al.* (2007) conducted combustion tube experiments using heavy oil from Mexico to evaluate the effect of catalysts on recovery during in situ combustion. For this study, two runs were carried out. The first run served as the control run with no catalysts while for the second run. The heavy oil was pre-mixed with the highly soluble organo-metallic catalysts (750ppm wt concentration) before loading into the combustion tube. The following observations were made from experimental results for the combustion run with catalysts in comparison with the control run:

1. Oil production acceleration
2. Increase in oil recovery
3. Higher combustion efficiency
4. A higher combustion front velocity
5. Sustained high temperatures during combustion

Ramirez *et al.* (2008) presented a study showing an increase in oil recovery from in situ combustion experiments with tetralin and nickel based catalyst. For the run with catalyst and tetralin, the tetralin and catalyst (nickel based) were pre-mixed with the heavy oil (12.5°API) from Mexico before loading into the combustion tube. Besides the increase in oil recovery observed in this run, there were other catalyst-improved qualities including:

1. Faster combustion run
2. Higher combustion efficiency
3. Reduction in sulphur, resins, and asphaltenes content of oils
4. Higher temperatures of about 600°C during combustion.

Ramirez noted that using an ionic based nickel solution at low concentration would result in an increase in oil recovery and also an upgrade in oil properties in situ.

Abuhesa and Hughes (2008) performed experiments to confirm the applicability of in situ combustion to catalytically upgrade a medium-heavy Clair oil (19.8°API), using a low pressure combustion cell. Experiments were conducted for both non-catalytic and catalytic procedures and for both dry and wet forward combustion processes. The study reported that produced oil from the non-catalytic experiments was thermally upgraded by 2 to 5 points depending on the experimental conditions, whereas produced oil from catalytic experiments showed an upgrade of 5 to 10 points. This significant difference was attributed to the combined effects of thermal and catalytic upgrading. The authors also reported that despite better upgrading characteristics of the catalytic experiments; oil recovery factor was less compared to the non-catalytic experiments. The experiments

also showed a reduction in the peak temperature, fuel consumption and air requirement for the wet in situ combustion process compared to the dry process. They concluded that the wet gas catalytic process achieved the highest oil recovery and upgrading characteristics.

In conclusion, previous work have shown that the addition of a combination of tetralin with metallic catalysts to the in situ combustion process have a significant impact on improving the quality and recovery of crude oil.

3 EXPERIMENTAL APPARATUS AND PROCEDURE

The five main components of the apparatus are the gas injection system, combustion tube, fluid production system, gas chromatograph, and the wet test meter system; and the data logging system. Each part of the equipment and the related experimental procedure are described in this section.

3.1 Experimental apparatus

3.1.1 Gas injection system

The gas injection system consists of two parts: nitrogen injection and air injection. Both paths are independent (through 1/4 in. tubing) and are opened or closed to the system with valves in the control panel. The injected nitrogen or air rate is controlled by a mass flow controller, installed before the injection pressure transducer. The 1/4 in. tubing line is reduced with Swagelok fittings to 1/8 in. tubing line, which is the gas inlet to the combustion tube.

3.1.1.1 Nitrogen injection

Nitrogen is used to flush the system before any combustion run allowing it to flow through the mass flow controller into the combustion tube. Nitrogen is also used to pressurize the combustion tube by closing the pressure regulator and the end of the production stream. At the end of the combustion run, nitrogen is injected into the system to flush and cool down the tube.

3.1.1.2 Gas injection

Air is injected at constant rate of 3 L/min throughout the combustion run. The air is purchased in cylinders, and is classified as dry and GC quality. The air injected must be of gas chromatography quality as air of low quality would reduce the accuracy of the readings obtained for these runs. The composition of air injected throughout the duration of the experimental runs. **Fig. 3.1** shows a schematic diagram of the experimental apparatus used for this research. The air filter removes all the impurities present in the air before it is injected into the combustion tube. This filter removes impurities such as dust that would affect the quality of the process. Data loggers as shown in **Fig. 3.1** determine the rate of air injected during the experiment. Other parameters shown by the data loggers include the volume of flue gas produced, the injection and production pressure, the distance of the combustion front from the top of the tube, and the temperatures of the combustion front at different distances along the combustion tube.

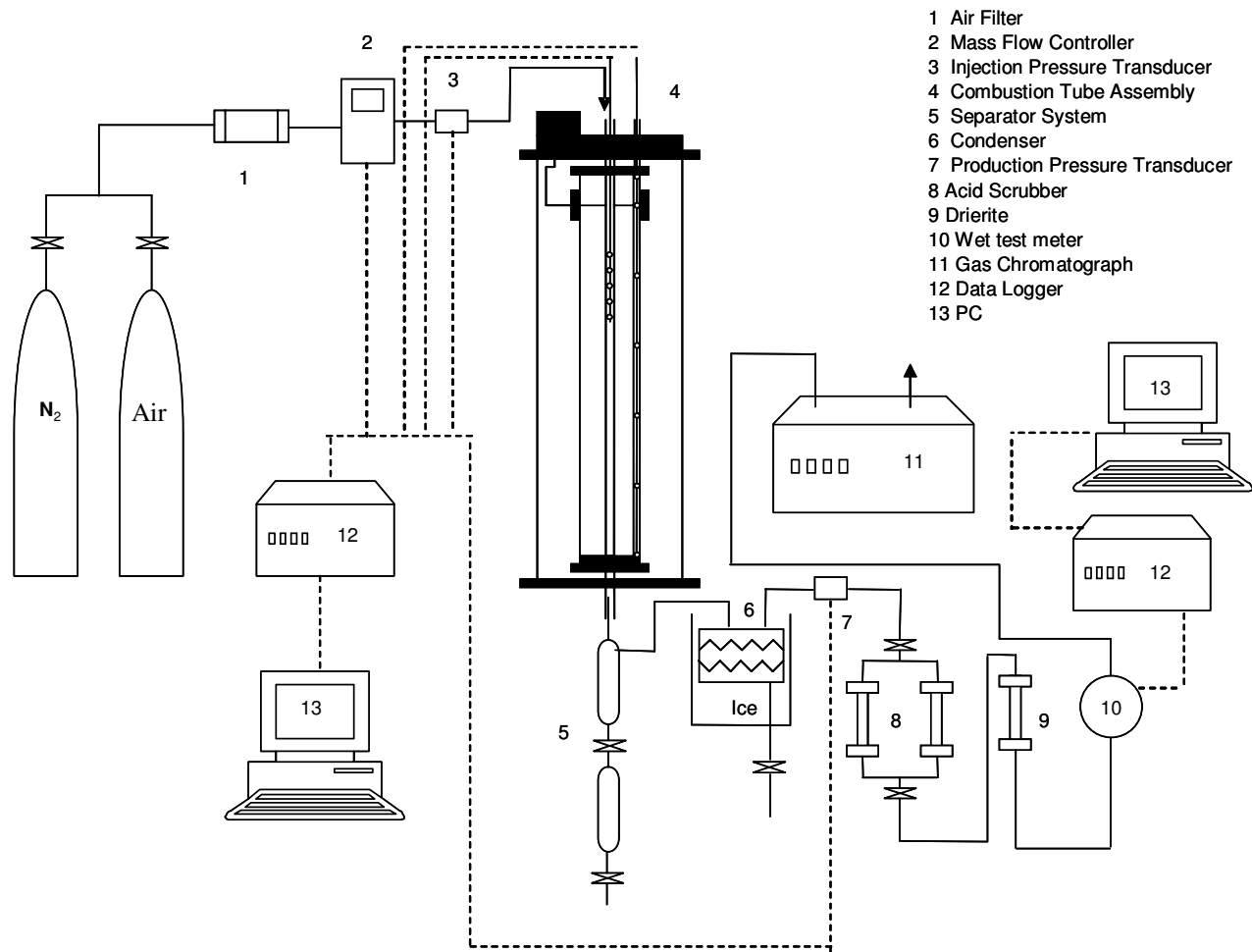


Fig. 3.1—Schematic diagram of experimental apparatus.

3.1.2 Combustion tube

The combustion tube (**Fig. 3.2**) is a stainless steel cylinder with an external diameter of 3 in. (7.62 cm), a wall thickness of 1/16 in. (0.16 cm) and a length of 40-1/8 in. (101.92 cm). Sharp-edged flanges seal the ends of the cell to copper gaskets. A 12-1/2 in long x 3/4 in. tube was silver soldered to the center of the top flange, and a 1 in. x 3/4 in. Swagelok fitting was machined and silver soldered to it. The assembly provided the path for the introduction of two 3/16 in. thermowells (**Fig. 3.3**), the one corresponding to a fixed set of thermocouples was 57-3/8 in. long, the other 56-1/2 in. long. Another tube, 10 in. long x 5/16 in. was soldered off-center on the top flange to allow air injection into the combustion tube through a reduction of Swagelok fitting to a 1/8 in. inlet. A 10 in. long x 5/16 in. tubing was silver soldered to the bottom flange of the combustion tube to allow the collection of fluids in the production system.

The combustion tube is placed inside the vacuum jacket (**Fig. 3.4**), a 6-1/2 in. internal diameter tube (8 in. external diameter) 46 in. long. The jacket is wrapped with electric band heaters and covered with a one inch thick insulation. Flanges seal the end of the vacuum jacket to rubber o-rings. A connection installed at the top flange of the jacket provides electric current to the resistance igniter, and drilled holes allow the insertion of the top tubing end of the combustion cell. The bottom flange also allows the insertion of the bottom end of the combustion cell and also provides a tubing connection for vacuum purposes. The vacuum jacket is isolated from the combustion cell with Teflon ferrules installed in both flange ends. The exterior of the vacuum jacket is an

aluminum cover with respective aluminum end caps. The center of the jacket is connected to a swivel that allows it to be rotated from the horizontal to vertical position.

One set of eight fixed J-type thermocouples (spaced 14.1 cm apart) runs through the assigned thermowell end and a set of six movable J-type thermocouples spaced 0.5 cm apart runs through the other end. All thermocouples used are 0.002 in. diameter. The set of eight thermocouples was inserted inside a 1/8 in. diameter x 63-1/2 in. long thermocouple sheath at the following depths: 1.4, 11.0, 25.1, 53.3, 67.4, 81.5, and 95.6 cm respectively measured from the top of the combustion tube. The other set of thermocouples was inserted inside a 1/8 in diameter x 62-1/8 in long thermocouple sheath. In this set the bottom thermocouple was set at 91.0 cm and the rest were spread 0.5 cm apart in a 2.5 cm length.

The combustion tube system is placed vertically and is secured to the production end and to the arm of the motor of the movable thermocouple set. Each one of the thermocouples is connected to its terminal to display or register its signal to the data logger and/or the control panel and/or PC monitor.

3.1.3 Fluid production system

A backpressure regulator (**Fig. 3.5**) maintains the outlet pressure of the combustion tube at a constant predetermined level during the experiment. The liquids leaving the combustion tube pass through a two-stage separator (**Fig. 3.6**) where they are collected at the production outlet.



Fig. 3.2—Combustion tube.



Fig. 3.3—Dual-thermowell assembly.

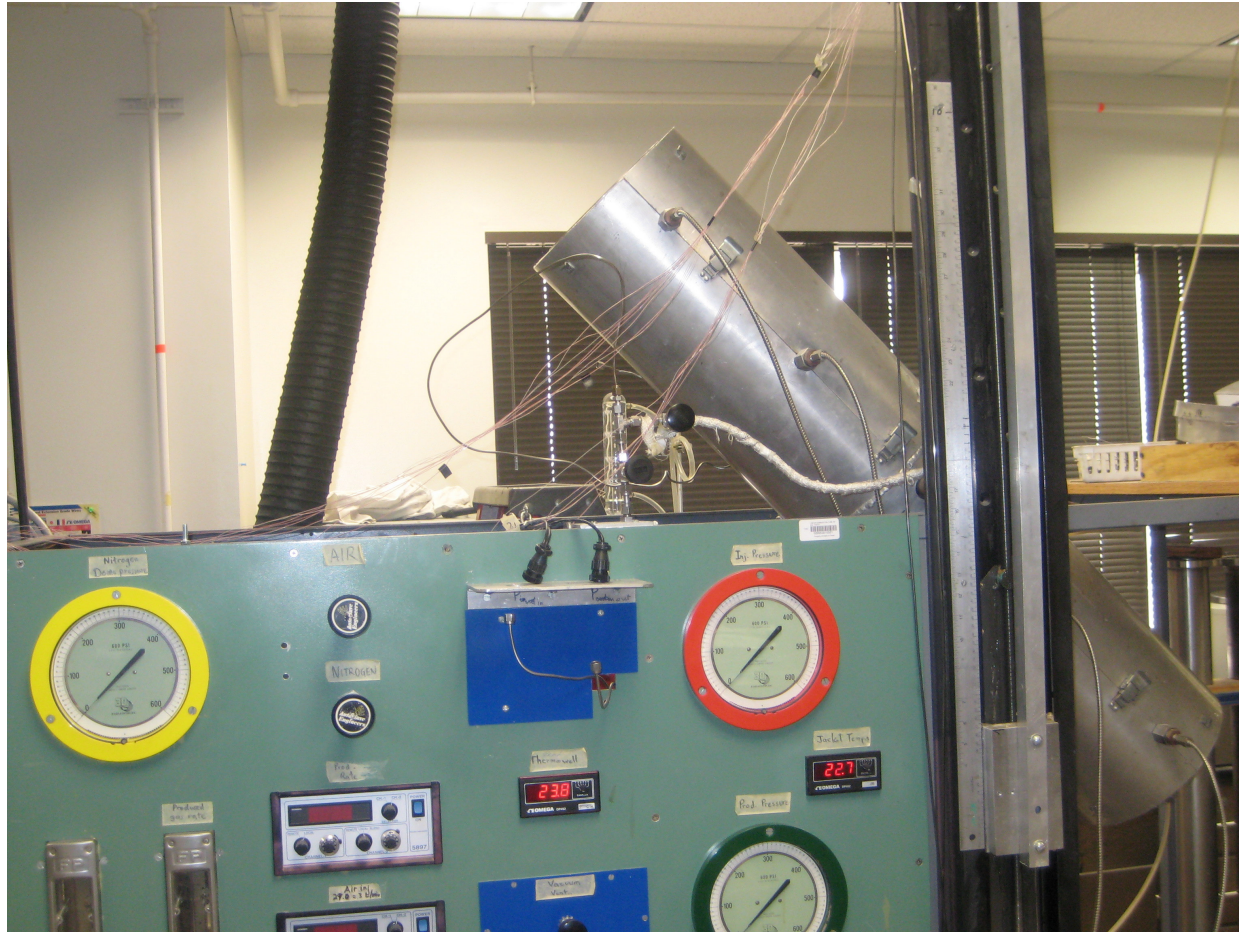


Fig. 3.4—Photograph showing vacuum jacket mounted behind the control panel.



Fig. 3.5—Part of panel showing inlet and outlet pressure gauges and back-pressure regulator at bottom.



Fig. 3.6—Two-stage separator with electric heater tape wrapped around it.



Fig. 3.7—Condenser unit to cool and condense liquids from produced gases.



Fig. 3.8—Acid scrubber and drierite columns.



Fig. 3.9—HP 5890 Series II gas chromatograph, HP 3966A integrator and VICI sequence programmer.



Fig. 3.10—Wet test meter.



Fig. 3.11—Data logger unit and PC.

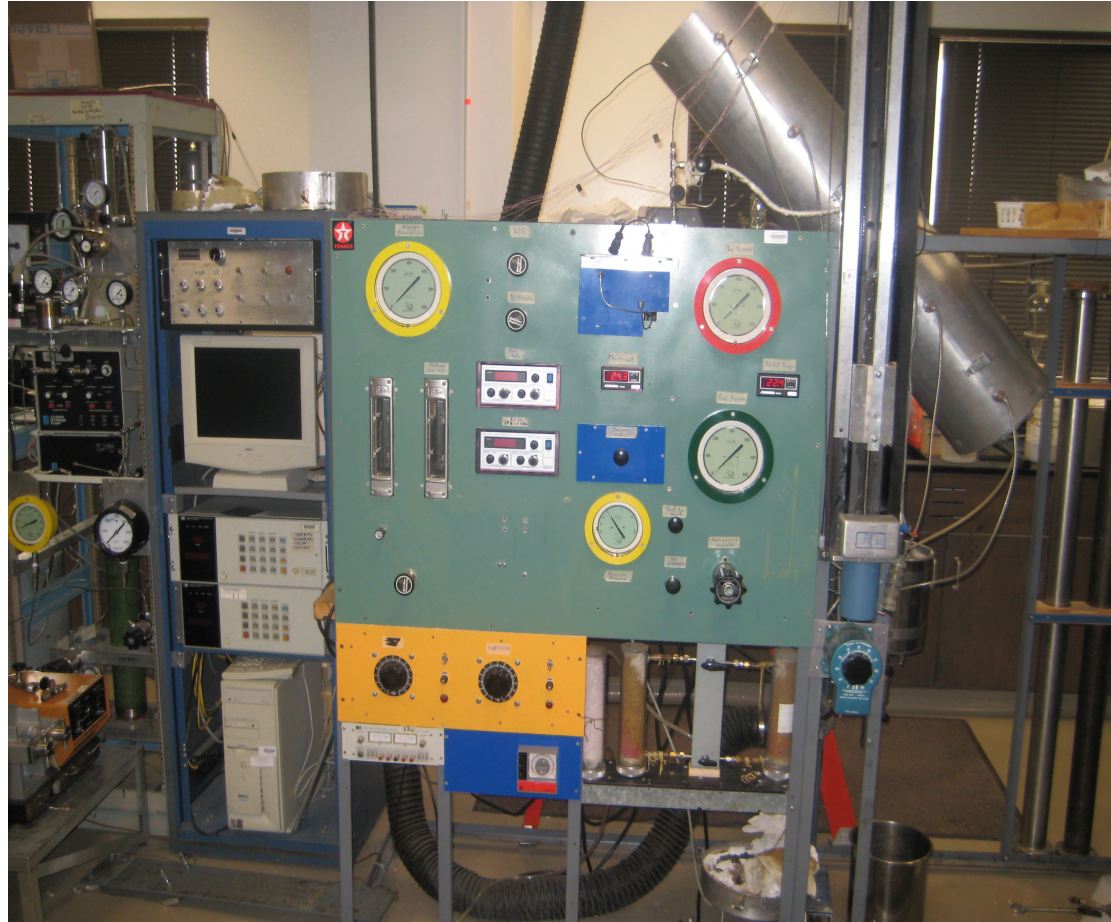


Fig. 3.12—Complete view of apparatus.



Fig. 3.13—Hobart A200 electric mixer.

Gases are passed through a condenser unit (**Fig. 3.7**) containing ice to recover any volume of liquid in this stream. Gases flowing to the gas chromatograph are scrubbed of acid, using a column of permanganate, and dehydrated, using a column of calcium sulfite, before entering the next system (**Fig. 3.8**).

3.1.4 Gas chromatograph and wet test meter system

A small fraction of produced gas is injected into the HP 5890 Series II gas chromatograph (**Fig. 3.9**) where the gas is analyzed for carbon dioxide, oxygen, nitrogen, and carbon monoxide every 15-20 minutes. This data is registered in a HP 3966A Integrator. A wet test meter (**Fig. 3.10**) installed before the gas chromatograph allows the measurement of the produced combustion gases, which is recorded in a PC.

3.1.5 Data measurement and recording system

Two data loggers and two personal computers (**Fig. 3.11**) are used to record the following parameters: time, jacket temperatures, fixed thermocouple temperatures, movable thermocouple temperatures, injection pressure, production pressure, depth of bottom movable thermocouple, gas injection rate, average produced gas rate, cumulative gas rate. The parameters are recorded at 30-second intervals and most of them are displayed on the PC monitors for monitoring purposes. A complete view of the apparatus can be seen in **Fig. 3.12**. The Hobart A200 electric mixer (**Fig. 3.13**) is used to obtain a homogeneous mixture just before tamping.

3.2 Experimental procedure

3.2.1 Preparation and loading of mixture for heavy oil runs

First, the bottom flange of the combustion tube was installed. Two 3/16 in. thermowells connected to meshed steel screens at the bottom, to prevent sand blocking, were introduced into the tube. After this, the top flange of the combustion tube was installed and the flange bolts fastened. Then the weight of the combustion tube was weighed. After this, the injection assembly was installed in preparation for a pressure test of the fastenings at the bottom of the flange. The cell was pressure tested for leaks at 100 psig for about 15 mins. Once the pressure test was successfully completed, the injection tube was loosened and the pressure in the combustion tube was allowed to drop to atmospheric. About 6500 g of sand was measured and placed in a mixing bowl. About 500 g of water was introduced into the mixing bowl and then thoroughly mixed using a small shovel. Then, about 440 g of oil premixed with 500 ppm ionic-based metallic catalyst and tetralin were added and mixed thoroughly until homogenous distribution was achieved. The final mixture was weighted to determine the loss due to mixing.

The bottom flange of the combustion tube was installed. After this, portions of about 200 g. of mixture were introduced into the tube once the combustion tube was safely fastened in a vertical position. A heavy metal plunger that passed through the thermowells was used to tamp the sample into the tube. The process of adding sample and tamping was repeated until the tube was filled to about 10 cm from the top. About 5 ml of linseed oil was placed on the top of the sample to accelerate ignition. The combustion tube was then filled to the top with clean 100-mesh sand. The sand acts as

an insulator thus preventing the heat from combustion from affecting the top flange of the combustion tube. The weight of the combustion tube filled with mixture was weighed and compared to the weight of the empty tube earlier measured to determine the amount of mixture in the combustion tube.

The top flange of the combustion tube was installed and the flange bolts fastened. The injection assembly was carefully installed, passing through the thermowells, and Teflon ferrules passed through them and tightened. Nitrogen was introduced at the injection inlet and with the outlet of the combustion tube plugged, the cell was pressure tested for leaks at 400 psig for 20 minutes. Once the pressure test was performed successfully, the outlet plug of the combustion cell was slowly opened and the pressure in the tube is allowed to drop to atmospheric. The injection assembly was dismantled and an electric igniter was placed and tightened at the exterior of the combustion tube at the same depth where the linseed oil was placed. The tube was then placed carefully inside the vacuum jacket which was tilted to about 30° from the horizontal to allow better handling of the combustion tube. The bottom flange of the combustion tube was wrapped with insulation and the bottom flange of the vacuum jacket was installed. The electric igniter was connected to the ignition terminals of the top flange of the vacuum jacket and the latter was tightened. The injection assembly was replaced in its position then the fixed and movable thermocouple sheaths were inserted in their respective thermowells. Teflon ferrules were tightened to the outlet and injection assembly to seal the vacuum jacket from the combustion tube. The vacuum jacket was placed in a vertical position and the outlet of the combustion tube fastened to the production section. The

movable thermocouple sheath was fixed to the motor arm and all thermocouples were connected to their terminals. The vacuum jacket was tested for thirty minutes with a vacuum of about -28 inches Hg. The injection line was connected to the assembly, and the vacuum jacket heater was set to about 140°F (60°C) and left overnight to allow the temperature of the sand mix to stabilize. A band heater set at 30°C was wrapped around the separator so as to ensure unobstructed flow of produced oil through the separator into the sample bottles.

3.2.2 Preparation of mixture for intermediate oil runs

The bottom flange of the combustion tube was installed. Two 3/16 in. thermowells connected to meshed steel screens at the bottom, to prevent sand blocking, were introduced into the tube. After this, the top flange of the combustion tube was installed and the flange bolts fastened. Then the weight of the combustion tube was weighed. After this, the injection assembly was installed in preparation for a pressure test of the fastenings at the bottom of the flange. The cell was pressure tested for leaks at 100 psig for about 15mins. Once the pressure test was successfully completed, the injection tube was loosened and the pressure in the combustion tube was allowed to drop to atmospheric.

Then the Texas crude oil was dewatered using the Shimato dewatering unit. The oil gravity was measured to be 22.0°API. The core was broken up by hand into small pieces. About 6500 g of the core pieces and 730 g of the dewatered Texas crude oil were placed in a large mixing bowl. Using a *Hobart A200* (**Fig. 3.13**) electric mixer,

the core and oil mixture was blended to obtain a uniform mixture. The final mixture was weighted to determine the loss due to mixing.

The bottom flange of the combustion tube was installed. After this, portions of about 200 g of mixture were introduced into the tube once the combustion tube was safely fastened in a vertical position. A heavy metal plunger that passed through the thermowells was used to tamp the sample into the tube. The process of adding sample and tamping was repeated until the tube was filled to about 10 cm from the top. About 5ml of linseed oil was placed on the top of the sample to accelerate ignition. The combustion tube was then filled to the top with 100-mesh clean sand. The weight of the combustion tube filled with mixture was weighed and compared to the weight of the empty tube earlier measured to determine the amount of mixture in the combustion tube.

The top flange of the combustion tube was installed and the flange bolts fastened. The injection assembly was carefully installed, passing through the thermowells, and Teflon ferrules passed through them and tightened. Nitrogen was introduced at the injection inlet and with the outlet of the combustion tube plugged, the cell was pressure tested for leaks at 400 psig for 20 minutes. Once the pressure test was performed successfully, the outlet plug of the combustion cell was slowly opened and the pressure in the tube is allowed to drop to atmospheric. The injection assembly was uninstalled and an electric igniter was placed and tightened at the exterior of the combustion tube at the same depth where the linseed oil was placed. The tube was then placed carefully inside the vacuum jacket which was tilted to about 30° from the horizontal to allow better handling of the combustion tube. The bottom flange of the combustion tube was

wrapped with insulation and the bottom flange of the vacuum jacket was installed. The electric igniter was connected to the ignition terminals of the top flange of the vacuum jacket and the latter was tightened. The injection assembly was replaced in its position then the fixed and movable thermocouple sheaths were inserted in their respective thermowells. Teflon ferrules were tightened to the outlet and injection assembly to seal the vacuum jacket from the combustion tube.

The vacuum jacket was placed in a vertical position and the outlet of the combustion tube fastened to the production section. The movable thermocouple sheath was fixed to the motor arm and all thermocouples were connected to their terminals. The vacuum jacket was tested for thirty minutes with a vacuum of about -28 inches Hg. The injection line was connected to the assembly, and the vacuum jacket heater was set to about 104°F (40°C) and left overnight to allow the temperature of the sand mix to stabilize.

3.2.3 Procedure for heavy and intermediate oil runs

Prior to the beginning of the experimental run, the mass flow controller was calibrated to the injection rate, the gas chromatograph was also calibrated, the bottom of the movable thermocouple sheath was raised to the linseed oil depth, and the sand pack was pressurized with nitrogen to 300 psig. Electric current was gradually introduced into the igniter using a variable power transformer. Approximately 90 minutes later, the temperature in the combustion tube at the igniter level (movable thermowell placed at the linseed oil depth) reached about 570°F (300°C) and air injection was initiated at 3 L/min.

A backpressure regulator was adjusted to maintain a tube outlet pressure of 300 psig. The movable thermocouple reading in the instruments panel and PC activated to record data was observed to increase rapidly to about 932°F (500°C), a clear indication that ignition occurred inside the combustion tube. Combustion gas composition was measured every 15-20 minutes; temperature profiles approximately every 2 in. (5 cm), and production liquids every 15-20 minutes. Accurate readings of temperature profiles were taken with the set of six movable thermocouples, spaced 0.5 cm from each other, which allowed the recording of 6 entries just behind and ahead of the combustion front. These entries were made by pressing the enter key on the PC component of the data logger.

Liquids were collected in graduated sample bottles which were capped for subsequent analysis. The end of the combustion run occurred when no oil production was attained, in other words, the sand pack was burned to the bottom flange of the combustion tube. Combustion runs varied between 6-7 hours, depending on the nature of catalyst used and the type of oil used.

4 EXPERIMENTAL CONDITIONS AND RESULTS

4.1 Experimental conditions

A general overview of the experimental conditions is presented in this section. A few parameters were kept constant through all the heavy oil runs so a comparison can be made between the runs 1, 2 and 3. The constant parameters include:

1. Initial cell temperature : 60°C
2. Air injection rate : 3 SL/min
3. Injection pressure: 300 psi
4. Production pressure: 300 psi
5. Oil saturation: For all runs involving the heavy oil from Mexico, the oil saturation was kept constant at 24%.
6. Rock porosity: 35%

The following runs will be discussed in details in the next section:

1. Run 1: Combustion of Mexico heavy oil but without tetralin and catalyts.
2. Run 2: Combustion of Mexico heavy oil with tetralin and nickel catalyst.
3. Run 3: Combustion of Mexico heavy oil with tetralin and iron catalyst.
4. Run 4: Combustion of Texas intermediate oil without tetralin and catalyts.

Table 4.1 below shows the properties of the sand pack for all the runs involving heavy oil.

Table 4.1—Sand pack properties of the Mexico heavy oil combustion runs

	Run 1	Run 2	Run 3
Weight of mixture, g	6977.6	6984.2	6981.2
Oil, wt %	6.4	6.4	6.4
Water, wt %	7.1	7.1	7.1
Sand wt %	86.6	86.5	86.6
S _o (%)	23.8	23.7	23.4
S _w (%)	25.3	25.6	25.7
S _g (%)	50.9	50.7	50.9
Ø (%)	35.2	35.2	35.2

4.2 Experimental results

Nelson and McNeil (1961) derived the following ratios as indicators for the efficiency of the in-situ combustion process.

Apparent hydrogen-carbon ratio: The apparent HC ratio, F_{HC} , may be calculated from the following expression, using measured gas composition.

$$F_{HC} = 4 \frac{[0.2682N_2 - (O_{2P} + CO_2 + CO/2)]}{(CO_2 + CO)} \dots\dots\dots (1)$$

Air-fuel ratio: Air-fuel ratio, F_{AF} , is determined from the following equation.

$$F_{AF} = \frac{379 * N_2 * 100}{(100 - O_2) * (CO + CO_2) * (12 + F_{HC})} \dots\dots\dots (2)$$

m-ratio: The m-ratio, m , is defined as follows and is calculated using measured fraction of CO and CO_2 in the produced gas.

$$m = \frac{CO}{(CO + CO_2)} \dots\dots\dots(3)$$

4.2.1 Combustion run no. 1 (Mexico heavy oil)

Fig. 4.1 shows the flue gas composition for run 1. The gas composition was observed to be variable as seen in the figure. The average compositions for CO₂, O₂, N₂ and CO during the run are 9.5%, 1.2%, 83.1% and 3.6% respectively. The apparent H-C, F_{AF} and *m*-ratios are illustrated in **Fig. 4.2**. The consistency of the *m*-ratio and the F_{AF} ratio indicate a fairly stable combustion during this run.

Fig. 4.3 shows the temperature profile during the run. The average combustion temperature which is 484°C indicates that low temperature oxidation reactions are almost non-existent in this run. Low temperature oxidation reactions are unwanted during the combustion reaction because they results in condensation reactions. These condensation reactions result in longer hydrocarbon chains therefore resulting in oil of higher viscosity. **Fig. 4.4** shows a plot of distance covered by the combustion front against time. The slope from the linear trendline gives a combustion front velocity of 15.1 cm/hr (0.5 ft/hr). Injection and production pressure are fairly constant throughout the run as indicated in **Fig. 4.5**. Average injection and production pressures are 306 psi and 306 psi respectively. **Fig. 4.5** also shows an almost constant air flow rate of an average value of 3.0 L/min during the run.

Cumulative oil and water production against time are shown in **Fig. 4.6**. Cumulative volume of oil is 430 cm³ which is 83% of the Original Oil-In-Place (OOIP) for this run as shown in **Fig. 4.7**. Water and oil are initially produced at 2.7 hrs and 3.9 hrs

respectively. **Fig. 4.8** shows the flue gas is produced at an average rate of 2.1 SL/min while the cumulative volume of gas produced is 855.7 SL. API gravity measured at the end of the run increased by an average of 3 points at all temperatures as shown in **Fig. 4.9**. These API gravity measurements are done at different temperatures (40°C, 50°C, and 60°C) to also determine the effect of temperature on the density of oil during the upgrading process. Also the upgrading effect was shown in **Fig. 4.10** where viscosity decreased for all the temperature measurements because of the increasing light hydrocarbon content during the combustion run. These viscosity measurements were taken at different times during the course of the experiment and also at different temperatures (40°C, 50°C, and 60°C). The most significant viscosity reading was that taken at the end of the combustion run. The number of hours expended on combustion varied for the various runs.

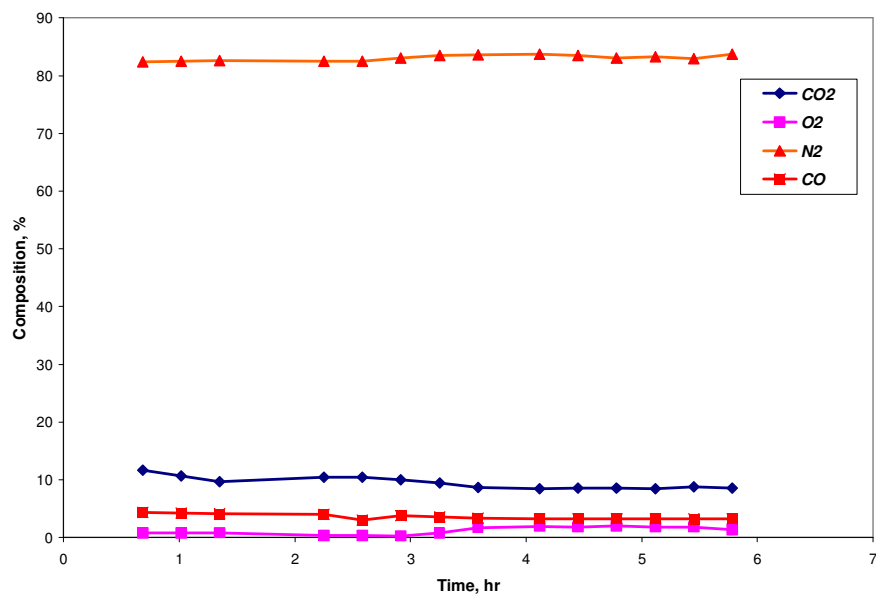


Fig. 4.1—Combustion gas composition for run no. 1.

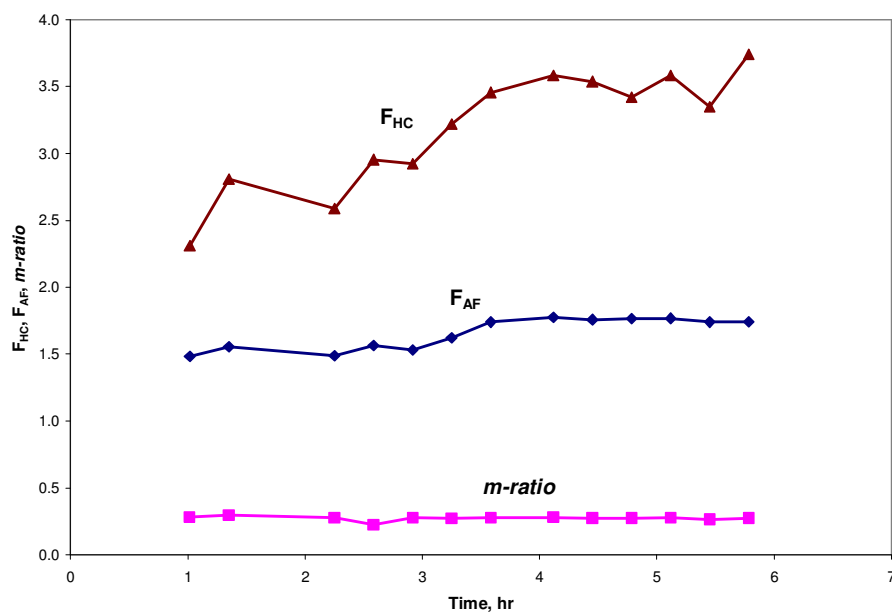


Fig. 4.2— F_{HC} , F_{AF} , m -ratio for run no. 1.

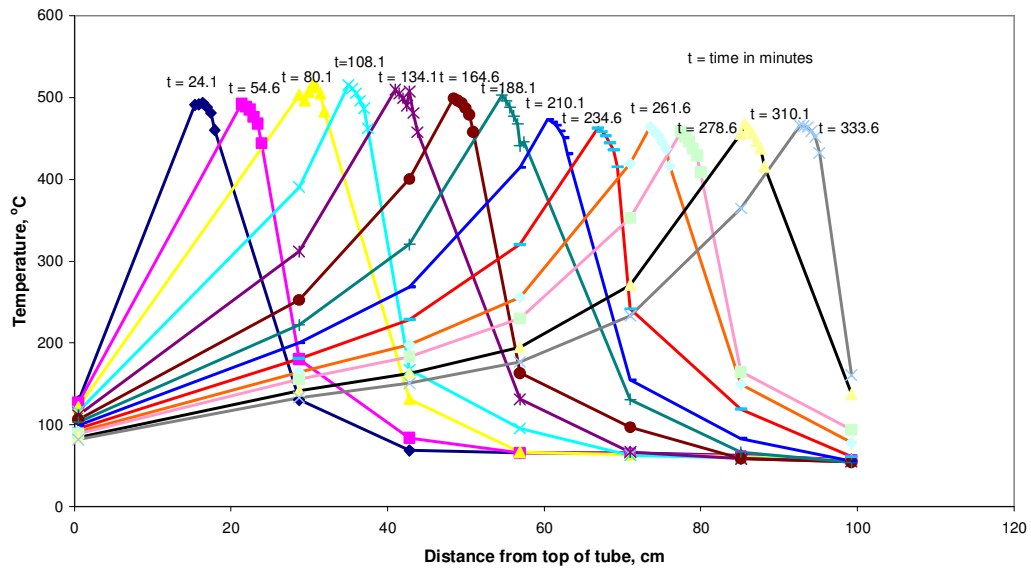


Fig. 4.3—Temperature profile for run no. 1.

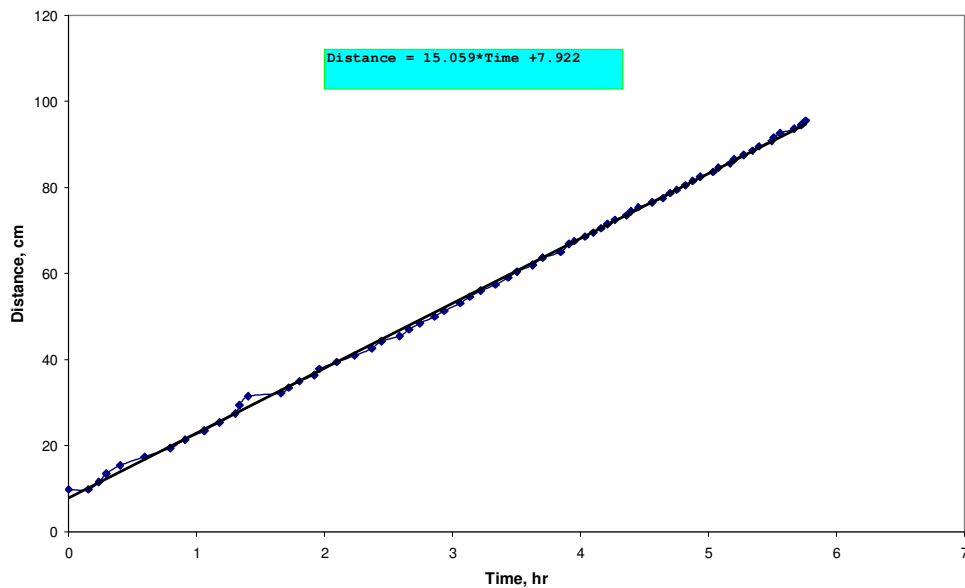


Fig. 4.4—Combustion front velocity for run no. 1.

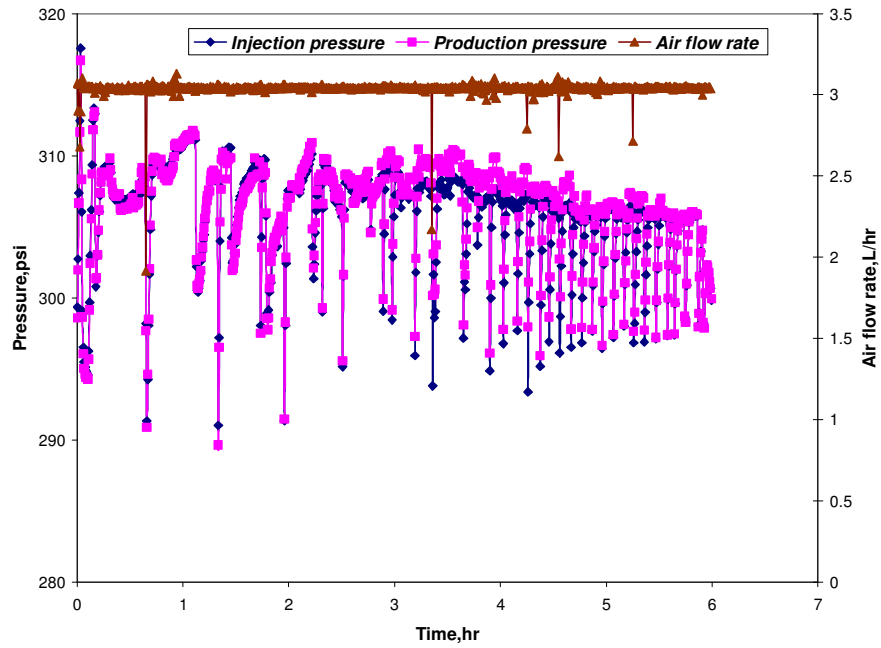


Fig. 4.5—Injection and production pressures and air flow rates for run no. 1.

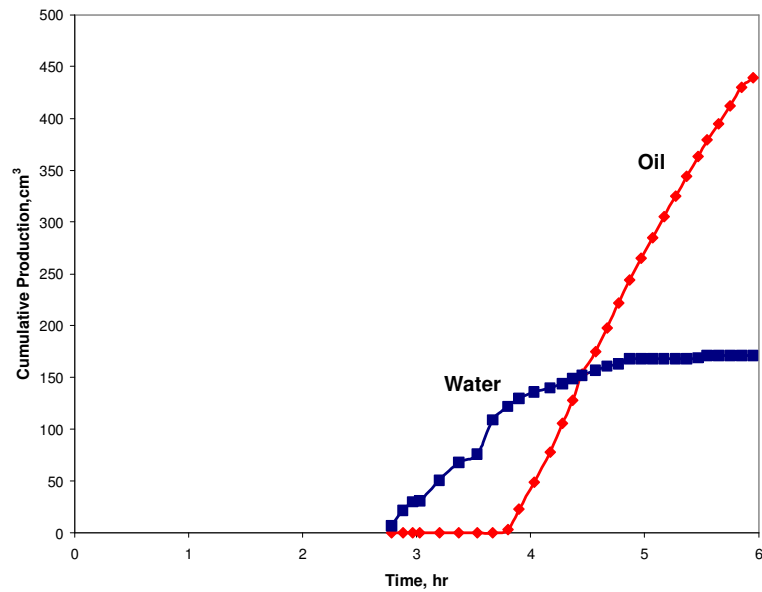


Fig. 4.6—Cumulative oil and water production for run no. 1.

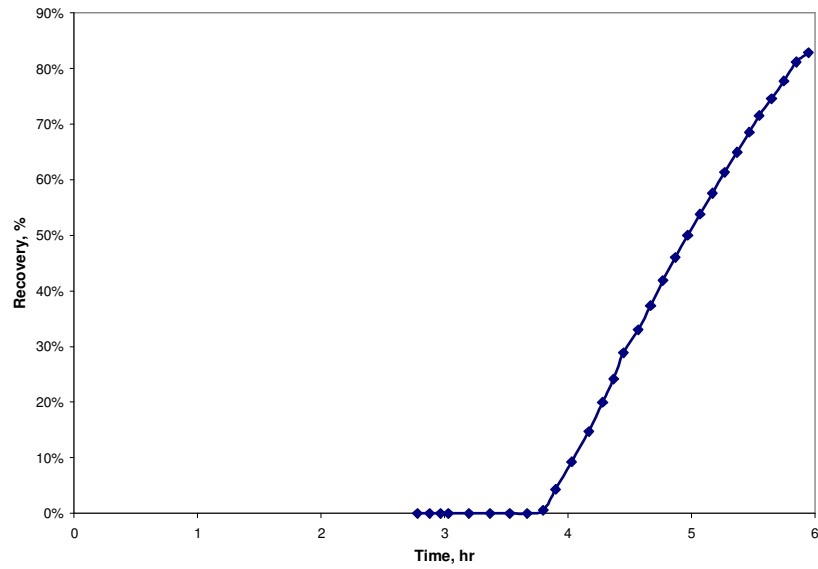


Fig. 4.7—Oil recovery for run no. 1.

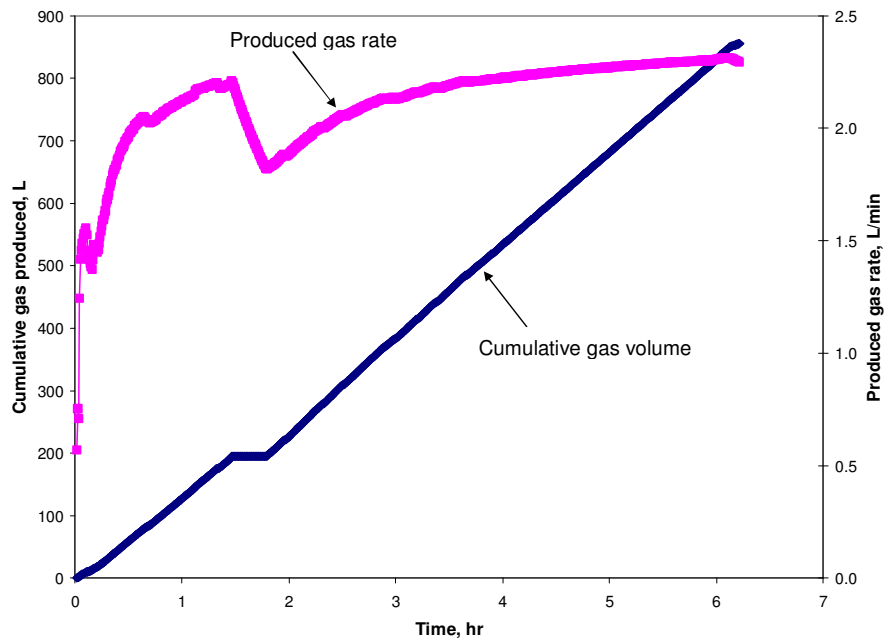


Fig. 4.8—Cumulative produced gas volume and produced gas rates for run no. 1.

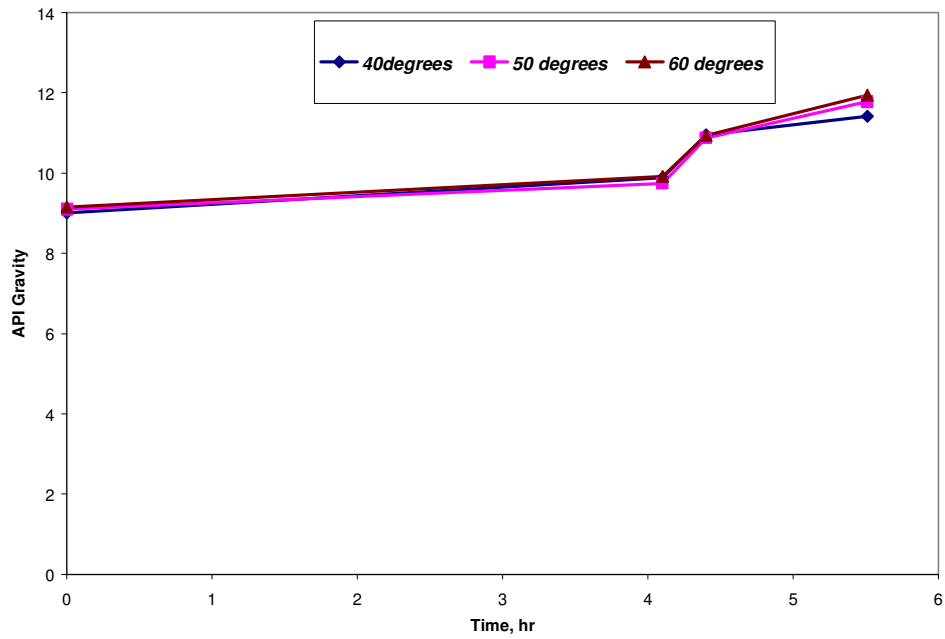


Fig. 4.9—Produced oil gravity at different temperatures for run no. 1.

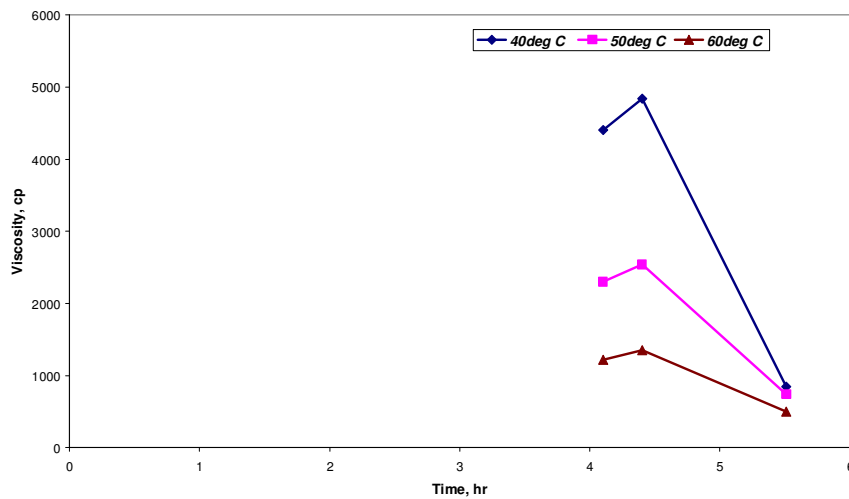


Fig. 4.10—Produced oil viscosity at different temperatures for run no. 1.

4.2.2 Combustion run no. 2 (Mexico heavy oil with tetralin and nickel)

The flue gas composition for run 2 is shown in **Fig. 4.11**. The composition of the gases was observed to be fairly constant indicating a higher level of stability compared to run 1. The average compositions of CO₂, O₂, N₂ and CO are 10.7%, 0.5%, 82.0% and 3.6% respectively. The low concentration of O₂ indicates a more efficient combustion compared to run 1. The apparent H-C ratio (F_{HC}), the m -ratio and the air-fuel ratio (F_{AF}) are shown in **Fig. 4.12**. Average values of 2.34, 0.25 and 1.47 were obtained for H-C ratio, m -ratio and the air-fuel ratio. The consistency of the m -ratio and the F_{AF} ratio indicate a more stable combustion during this run compared to run 1.

The temperature profile of this run is shown in **Fig. 4.13**. The average combustion temperature is 501°C shows improved combustion compared to run 1. Low temperature oxidation reactions are unwanted during the combustion reaction because it results in condensation reactions. These condensation reactions results in longer hydrocarbon chains therefore resulting in oil of higher viscosity. This can be attributed to the catalyst which lowers the activation energy required for combustion. The combustion front velocity is obtained from **Fig. 4.14**, a plot of distance covered by combustion front against time, to be 13.0 cm/hr (0.43 ft/hr). The injection and production pressures are plotted versus time in **Fig. 4.15**. The average injection and production pressures through the run are 304 psi and 304 psi while air was injected at an average rate of 3.0 SL/min throughout the run.

Fig. 4.16 shows the cumulative volume of oil and water, with an initial oil and water production time of 1.1 hrs and 3.8 hrs correspondingly. Cumulative volume of oil is

446.7 cm³ which is 90% of the Original Oil-In-Place (OOIP) for this run as shown in **Fig. 4.17**. The flue gas is produced at an average rate of 2.4 SL/min while the cumulative volume of gas produced is 804.7 SL (**Fig. 4.18**). Produced oil gravity at 60°C at the end of run no. 2 was 4 points higher than initial API gravity as presented in **Fig. 4.19**. These API gravity measurements are done at different temperatures (40°C, 50°C, and 60°C) to also determine the effect of temperature on the density of oil during the upgrading process.

The viscosity of the produced oil dropped to 367 cp from its initial value of 1176 cp as shown in **Fig. 4.20**. These viscosity measurements were taken at different times during the course of the experiment and also at different temperatures. The most significant viscosity reading was that taken at the end of the combustion run. The number of hours expended on combustion varied for the various runs.

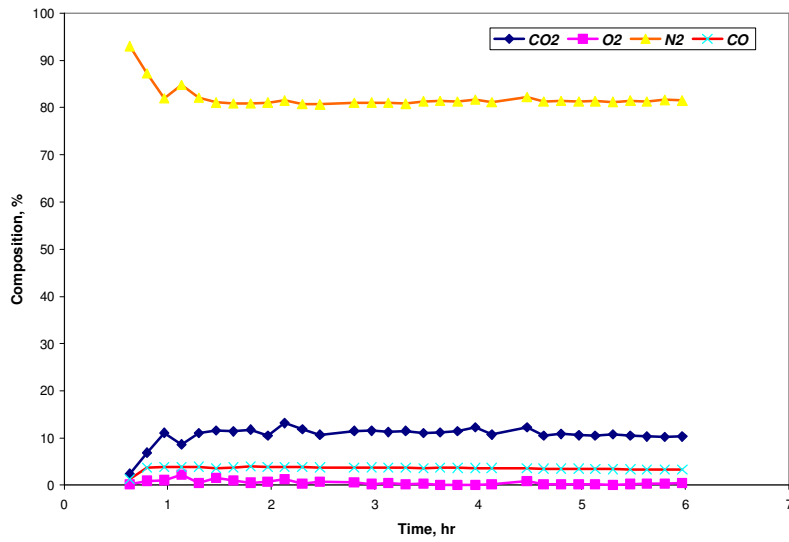


Fig. 4.11—Combustion gas composition for run no. 2.

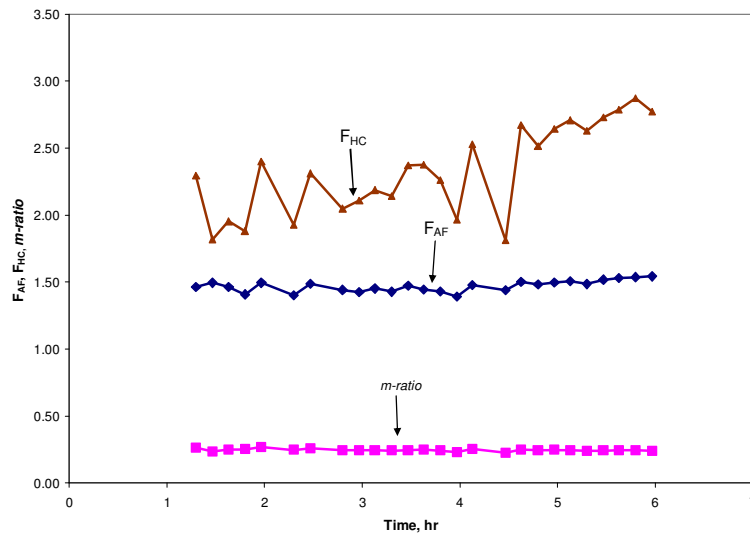


Fig. 4.12— F_{HC} , F_{AF} , m -ratio for run no. 2.

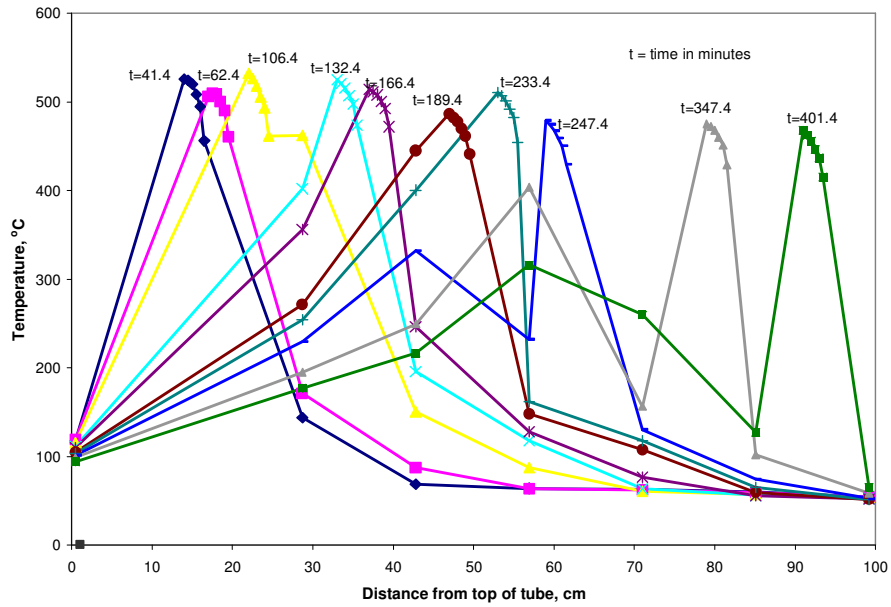


Fig. 4.13—Temperature profile for run no. 2.

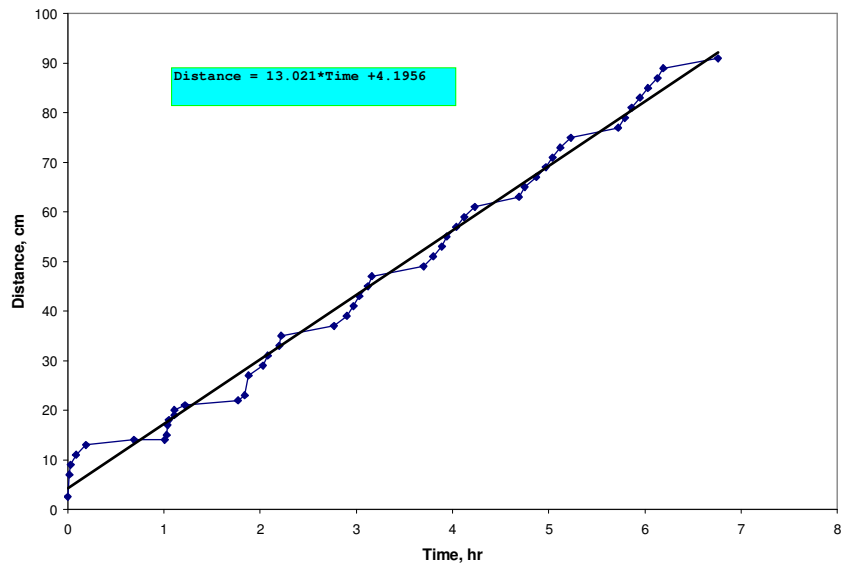


Fig. 4.14—Combustion front velocity for run no. 2.

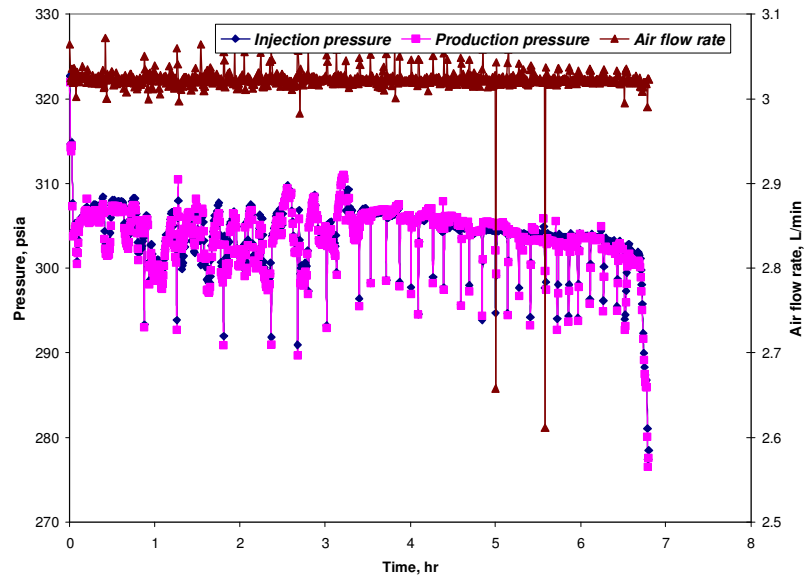


Fig. 4.15—Injection and production pressures and air flow rates for run no. 2.

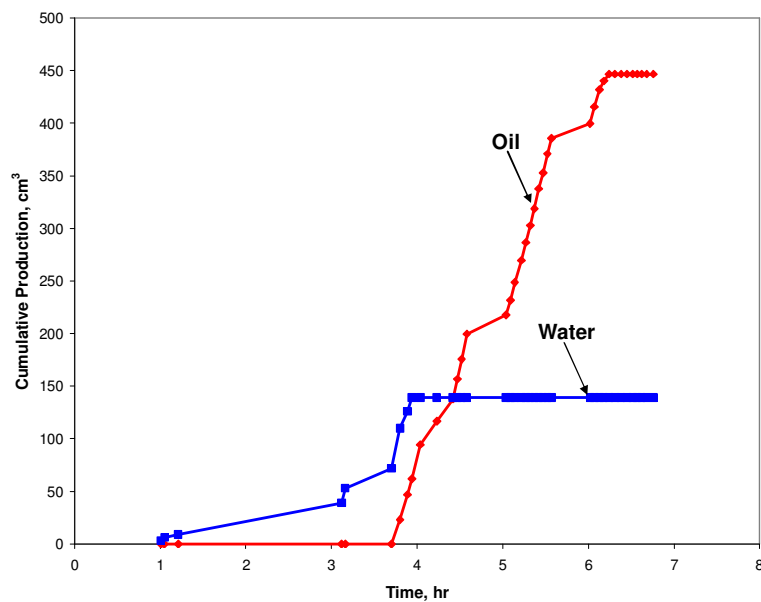


Fig. 4.16—Cumulative oil and water production for run no. 2.

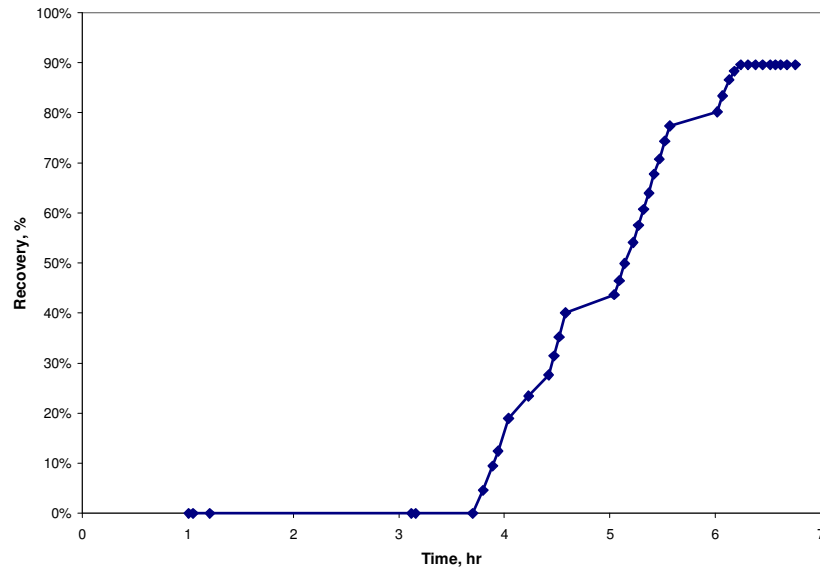


Fig. 4.17—Oil recovery for run no. 2.

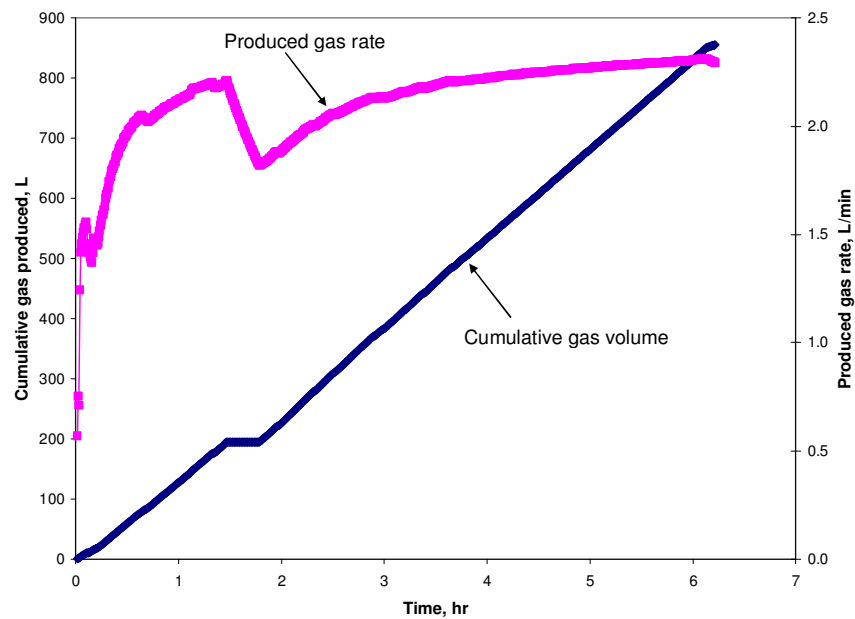


Fig. 4.18—Cumulative produced gas volume and produced gas rate for run no. 2.

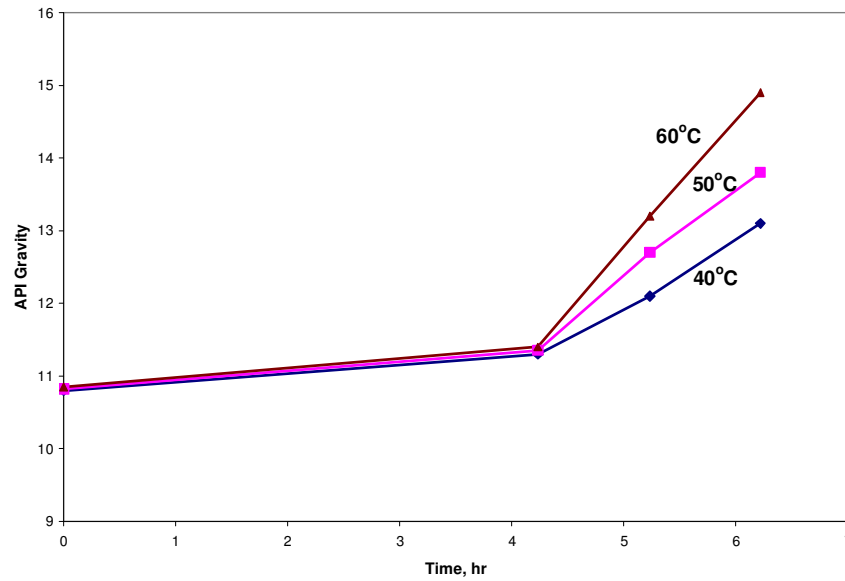


Fig. 4.19—Produced oil gravity at different temperatures for run no. 2.

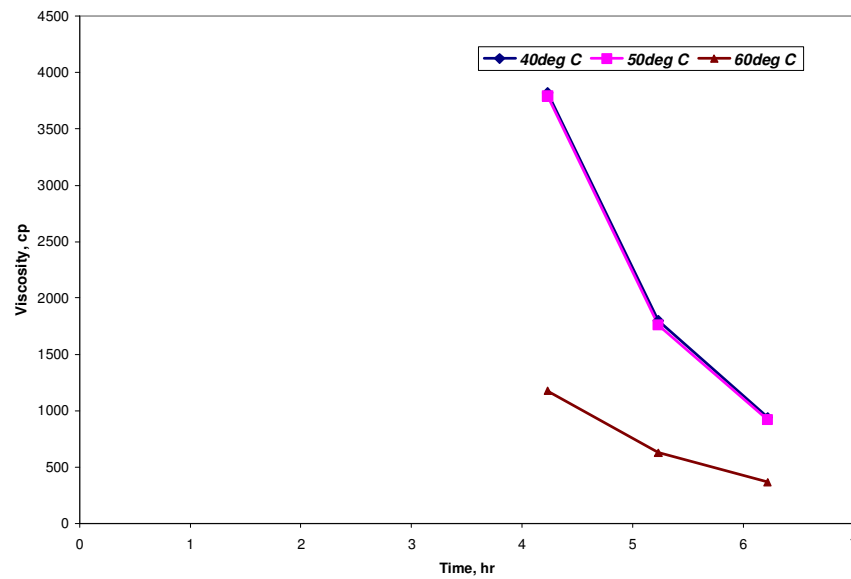


Fig. 4.20—Produced oil viscosity at different temperatures for run no. 2.

4.2.3 Combustion run no. 3 (Mexico heavy oil with tetralin and iron catalyst)

Stable combustion gas composition was also observed during this run as shown in **Fig. 4.21**. Average flue gas concentrations were N₂, 82.5%; CO₂, 12.45; O₂, 1.2% and CO, 4.0%. **Fig. 4.22** presents the apparent H-C ratio (F_{HC}), air-fuel ratio (F_{AF}), and the m -ratio. The apparent H-C ratio increases for the first 4 hrs then begins to drop till the end of the combustion process. This may be because of the low temperature oxidation ahead of the combustion front. The m -ratio and air-fuel ratio also show a similar trend to run 2 indicating stable combustion. The average values obtained were m -ratio, 0.25; F_{HC} , 1.69; and F_{AF} , 1.43.

The average combustion temperature for this run 492°C as obtained from the temperature profile presented in **Fig. 4.23**. Low temperature oxidation reactions are unwanted during the combustion reaction because it results in condensation reactions. These condensation reactions result in longer hydrocarbon chains which result in oil of higher viscosity. The combustion front velocity is obtained from **Fig. 4.24**, a plot of distance covered by combustion front against time, to be 14.1 cm/hr (0.46 ft/hr). The injection and production pressures are plotted versus time in **Fig. 4.25**. The average injection and production pressures through the run are 304 psi and 305 psi while air was injected at an average rate of 3.0 SL/min throughout the run.

Cumulative volumes of produced oil and water as presented in **Fig. 4.26** show initial oil production occurring at 2.0 hrs and initial water production at 3.37 hrs which is slightly lower than the two previous runs. Cumulative volume of oil produced is 509 cm³ which is 86% of the Original Oil-In-Place (OOIP) as presented in **Fig. 4.27**. **Fig. 4.28**

shows the cumulative gas volume of 844 L. Produced oil gravity at the end of the combustion run was 5.7°API higher than that of the original crude oil run at 60°C as shown in **Fig. 4.29**. These API gravity measurements were done at different temperatures (40°C, 50°C, and 60°C) to determine the effect of temperature on the density of oil during the upgrading process. API gravity measurements were also made at different times during the course of the experiments and then compared to the measurement at the beginning of the experiment.

The upgrading effect of the iron catalyst is also reflected in the decrease of viscosity by about 200 cp as shown in **Fig. 4.30**. These viscosity measurements were taken at different times during the course of the experiment and also at different temperatures. The most significant viscosity reading was that taken at the end of the combustion run. The number of hours expended on combustion varied for the various runs. Results showed that the number of hours for each experiment depended on the catalyst used for the run.

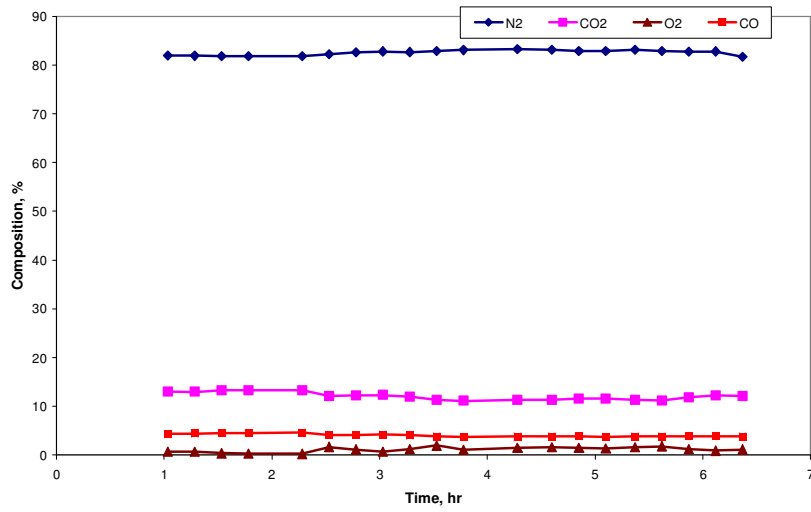


Fig. 4.21—Combustion gas composition for run no. 3.

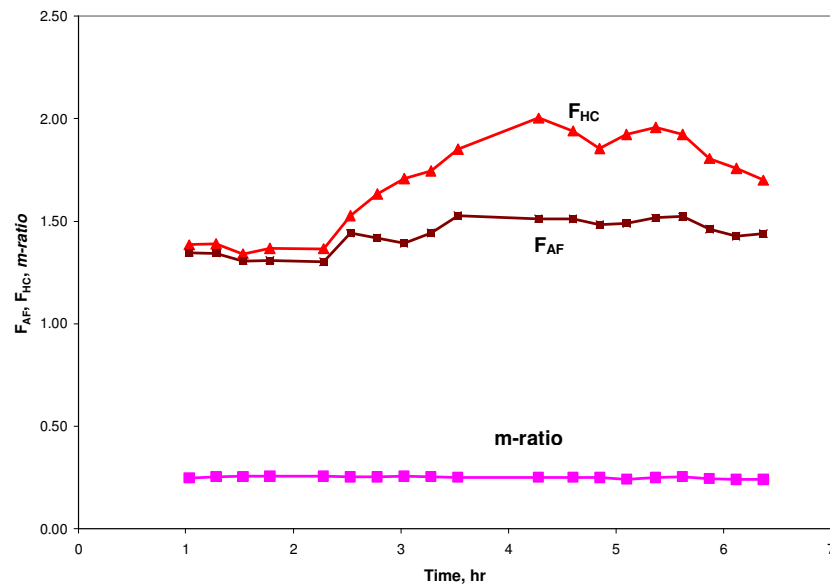


Fig. 4.22—F_{HC}, F_{AF}, *m*-ratio for run no. 3.

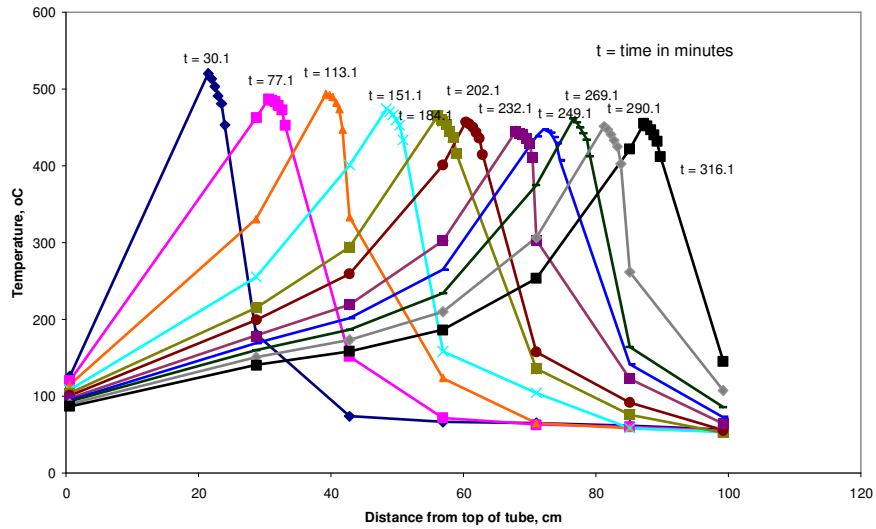


Fig. 4.23—Temperature profile for run no. 3

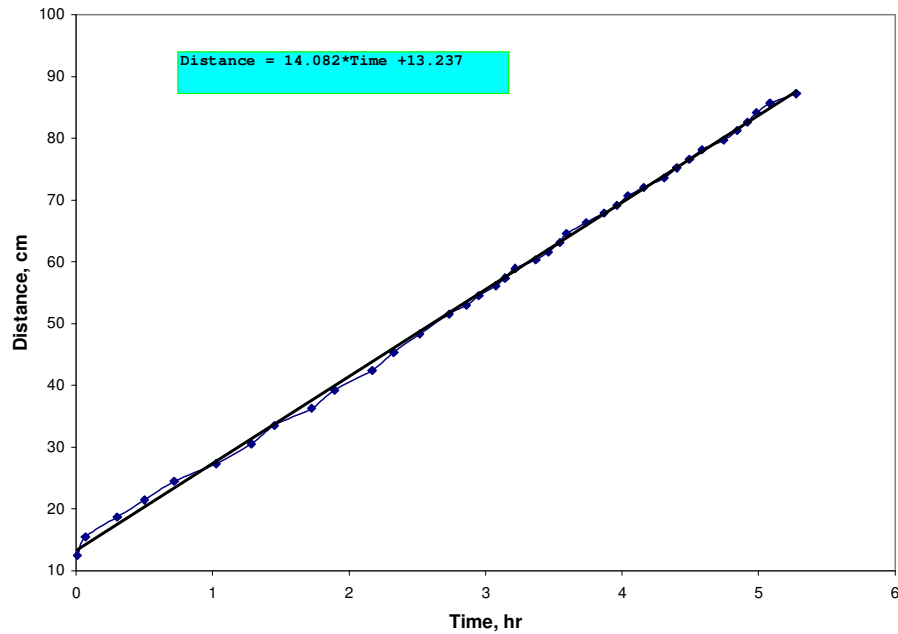


Fig. 4.24—Combustion front velocity for run no. 3.

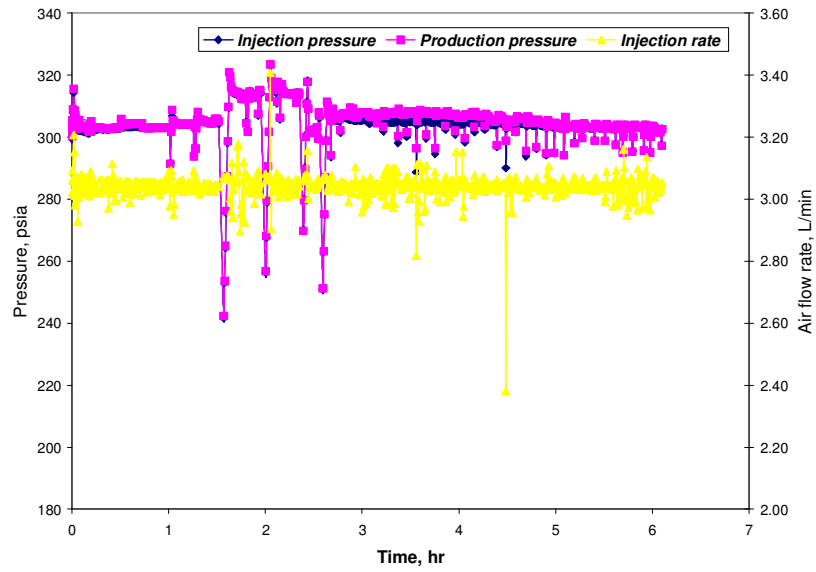


Fig. 4.25—Injection and production pressures and air flow rates for run no. 3.

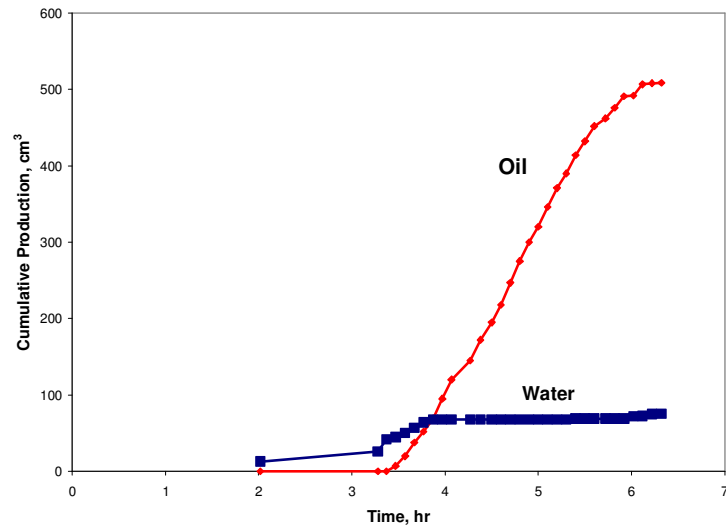


Fig. 4.26—Cumulative oil and water production for run no. 3.

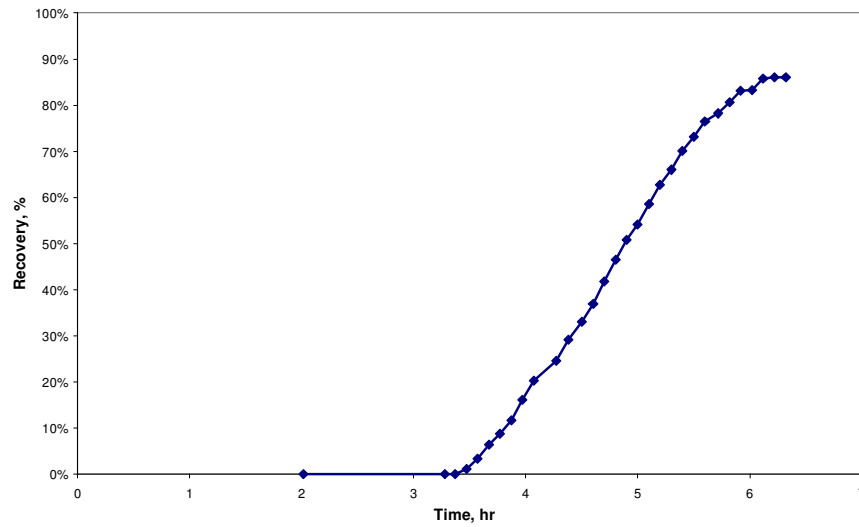


Fig. 4.27—Oil recovery for run no. 3.

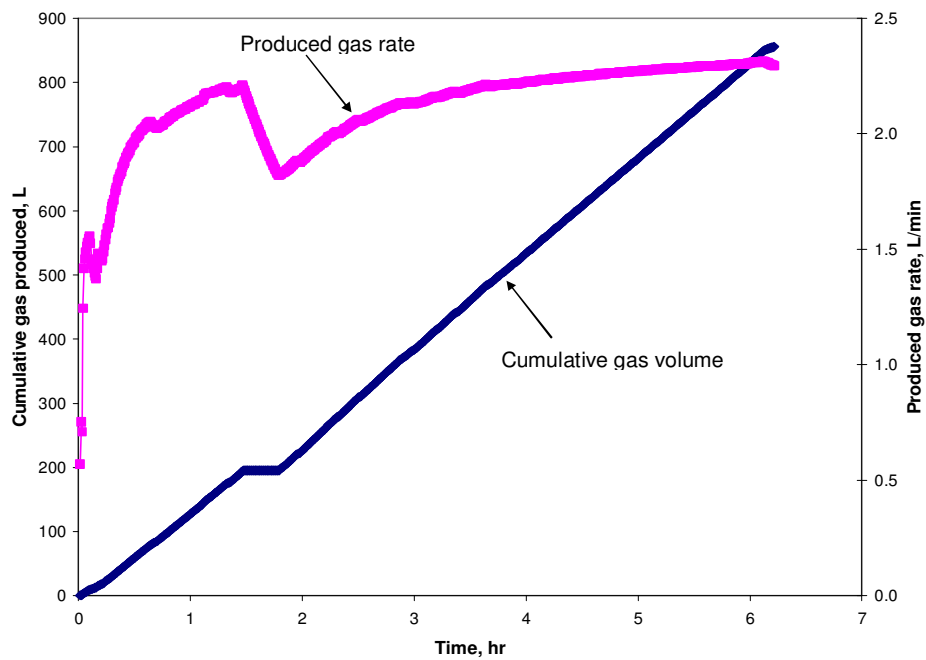


Fig. 4.28—Cumulative produced gas volume and produced gas rate for run no. 3.

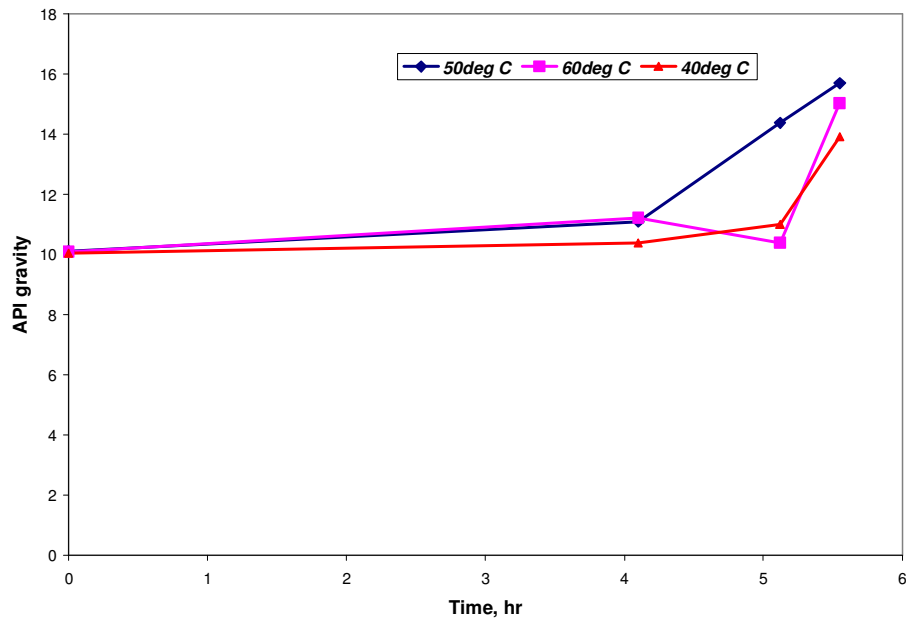


Fig. 4.29—Produced oil gravity at different temperatures for run no. 3.

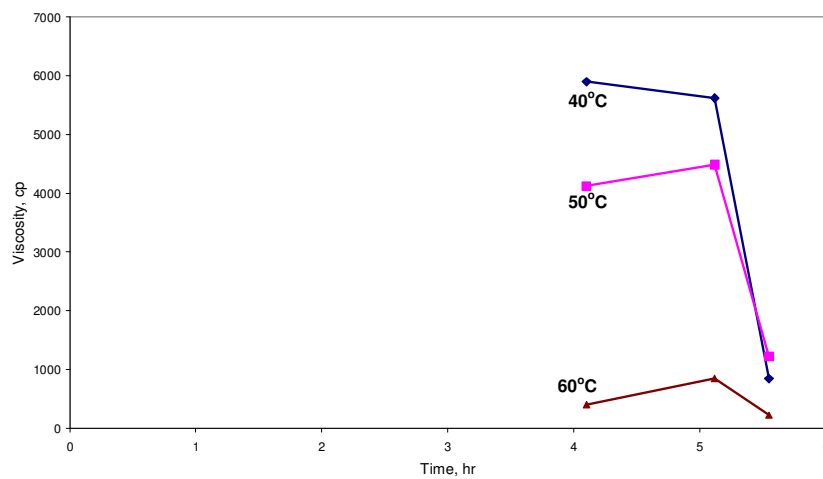


Fig. 4.30—Produced oil viscosity at different temperatures for run no. 3.

4.2.4 Combustion run no. 4 (Texas intermediate oil)

Produced gas composition as presented in **Fig. 4.31** indicates stable combustion. During the run, average produced gas concentrations were: CO₂, 13.4%; O₂, 0.7%; N₂, 80.5%; and CO, 3.5%. The average values of apparent H-C ratio, *m*-ratio and air-fuel ratio were 1.36, 1.37, and 0.21 respectively. These values are shown on **Fig. 4.32**.

The average combustion temperature during the run was 520°C (**Fig. 4.33**), confirming that the combustion was a high-temperature oxidation process. The average combustion front velocity was 0.30 cm/min (18.1 cm/hr) as observed in **Fig 4.34**. Injection and production pressures were maintained at 300psig throughout the run as shown in **Fig. 4.35**.

Fig. 4.36 shows the cumulative volumes of produced oil, with an initial oil production occurring at 4.00 hrs. The run lasted 7 hrs and 16 minutes. **Fig. 4.37** shows an oil recovery of 67% of original oil in the tube. Injected air rate was held at 3 SL/min, production pressure maintained at 300 psig. **Fig. 4.38** shows the cumulative gas volume of 1200 L.

Oil gravity at the end of the combustion run was 28.1°API which is 6.1°API higher than that of the original intermediate crude oil (**Fig. 4.39**).

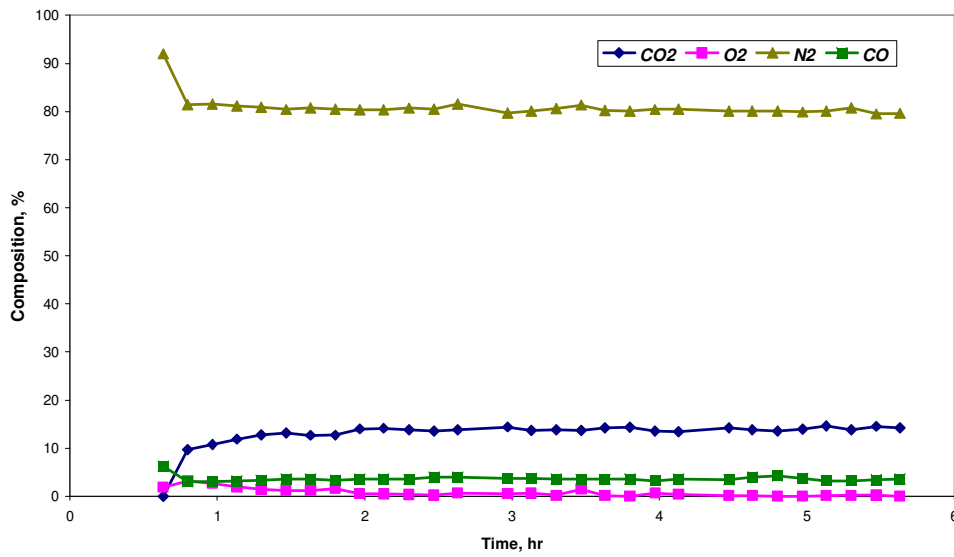


Fig. 4.31—Combustion gas composition for run no. 4.

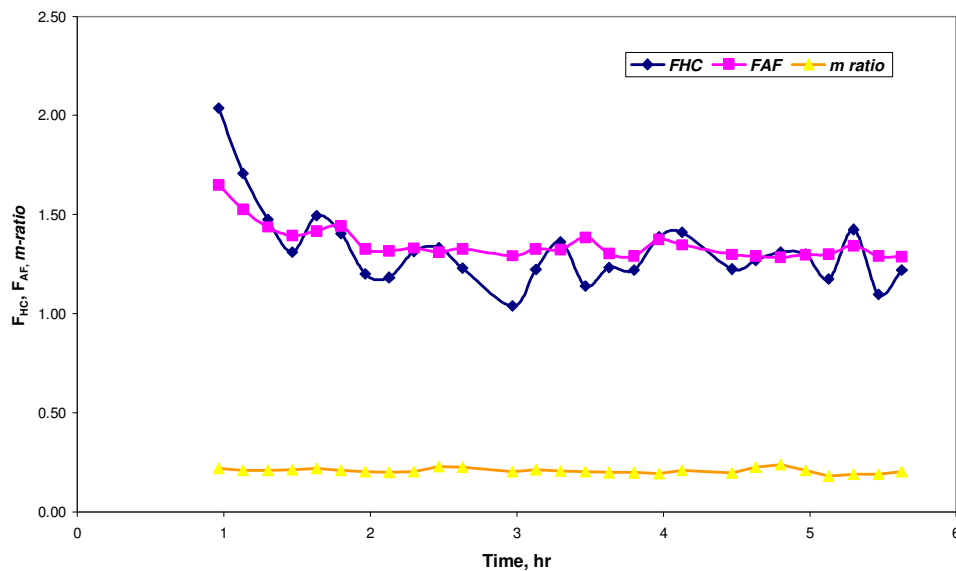


Fig. 4.32—FHC, FAF, m -ratio for run no. 4.

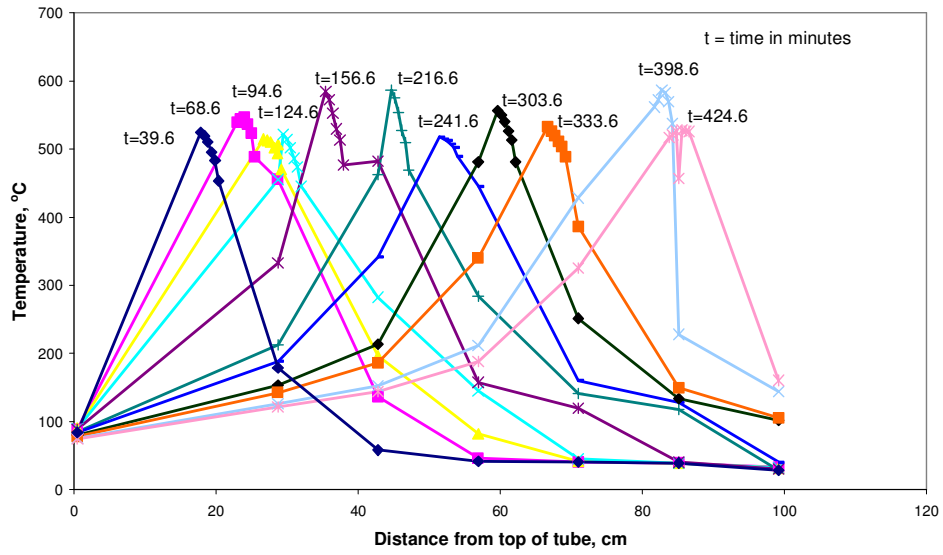


Fig. 4.33—Temperature profile for run no. 4.

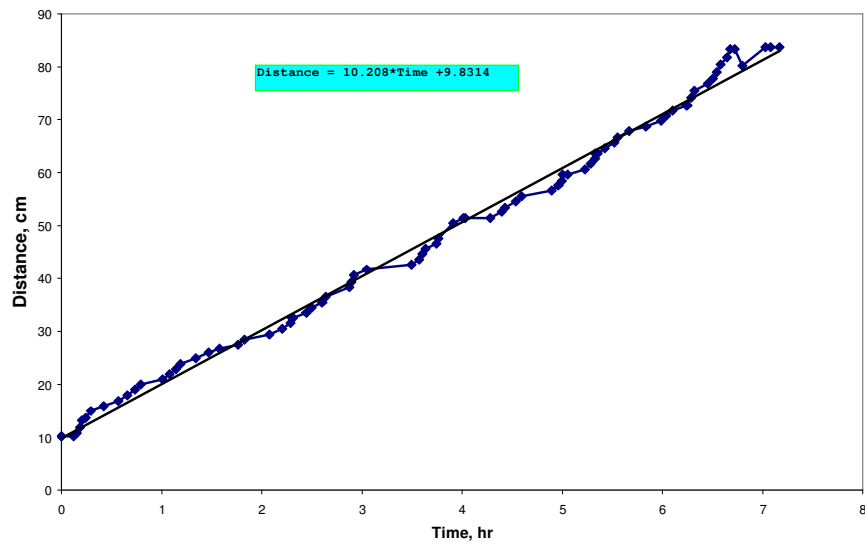


Fig. 4.34—Combustion front velocity for run no. 4.

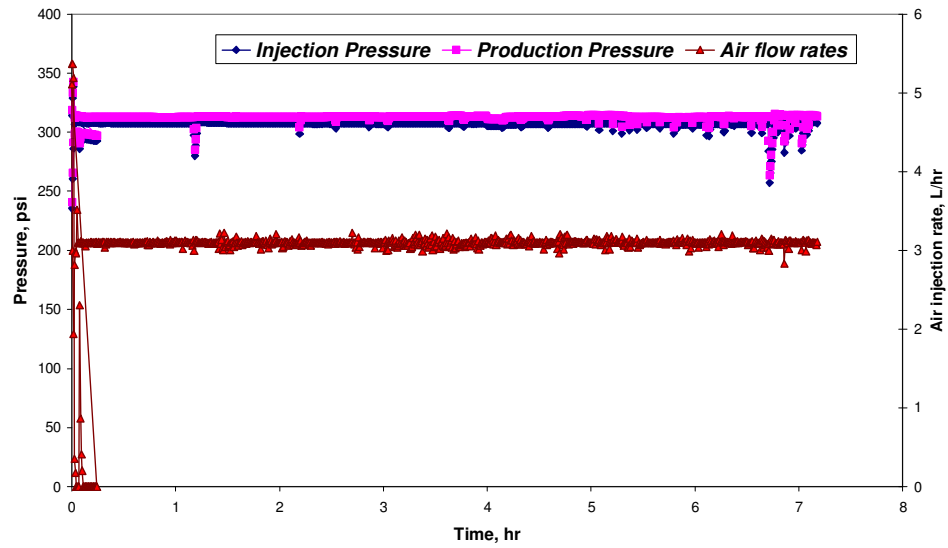


Fig. 4.35— Injection, production pressure and air flow rates for run no. 4.

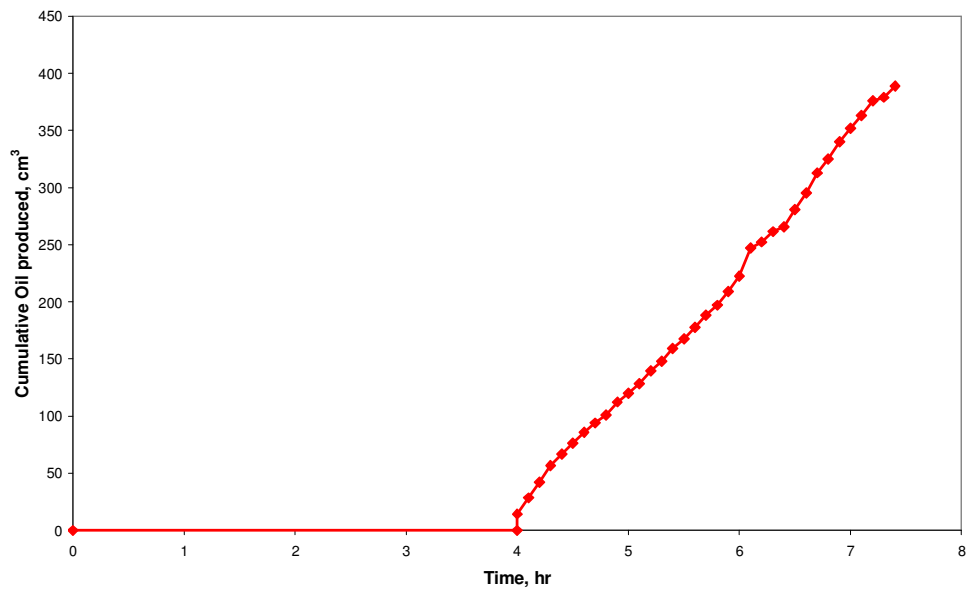


Fig. 4.36—Cumulative oil production for run no. 4.

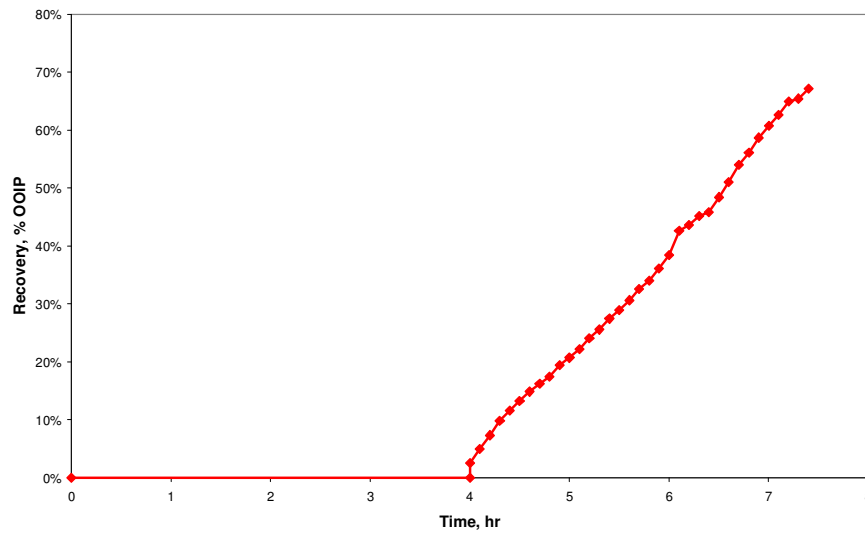


Fig. 4.37—Oil recovery for run no. 4.

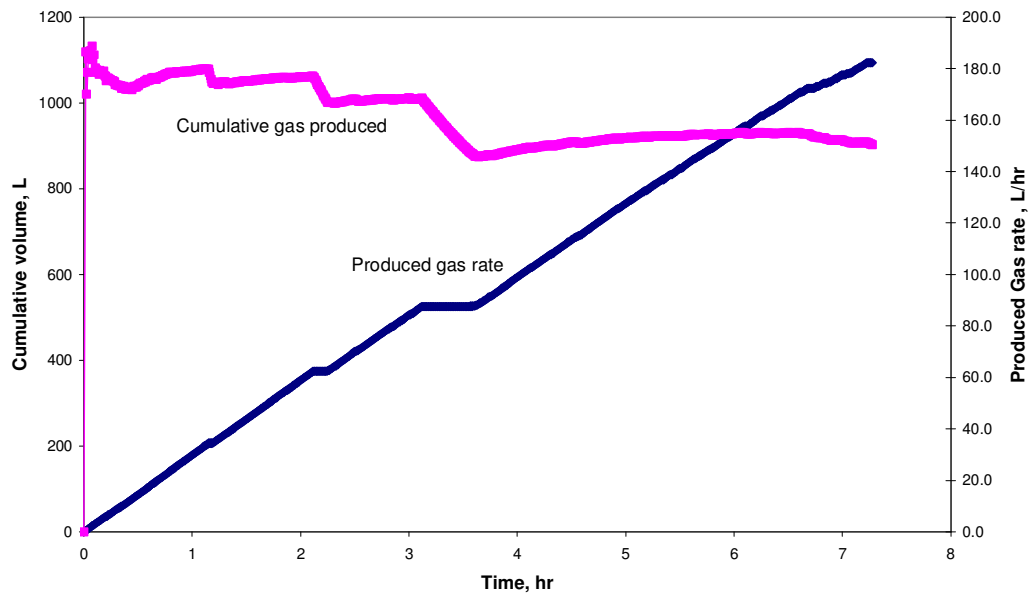


Fig. 4.38—Cumulative produced gas volume and produced gas rates for run no. 4.

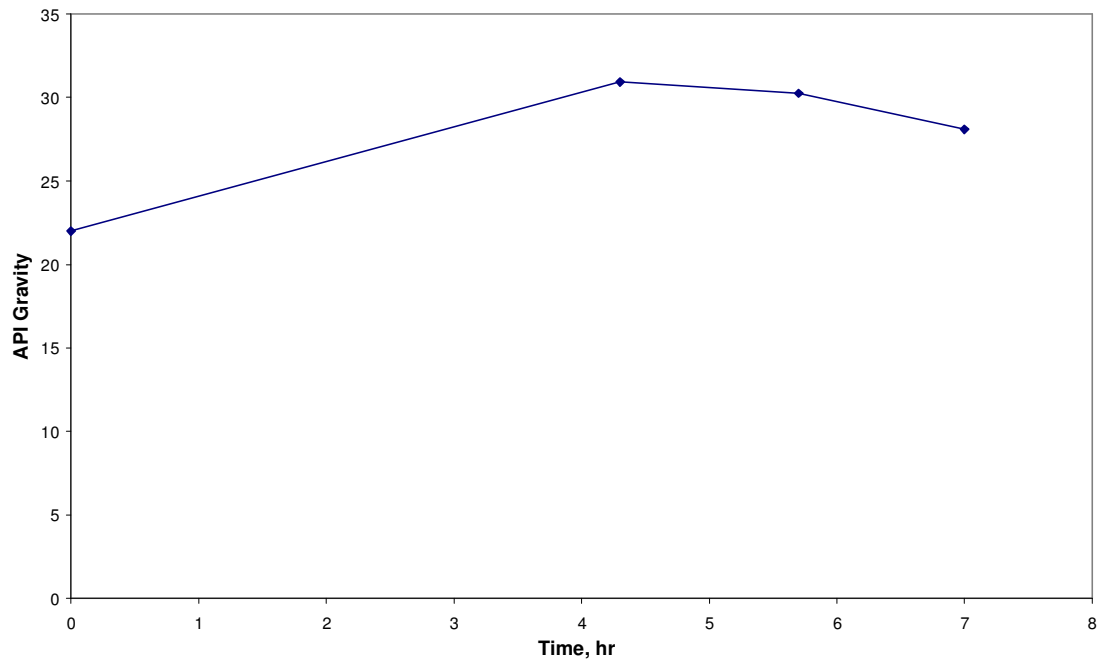


Fig. 4.39—Produced oil gravity for run no. 4.

4.3 Comparison of runs (Mexico heavy oil)

For all the runs involving heavy oil from Mexico, we compared the recovery factors to evaluate the effectiveness of the combination of tetralin and metallic catalysts on in-situ combustion. **Fig. 4.40** shows that the recovery factor for Run 2 is 7 points more than run 1 while the recovery factor for Run 3 is 3 points more than run 1.

A comparison of the upgrading effect of the different catalysts was determined from a plot of API gravity at 60°C of produced oil against time as shown in **Fig. 4.41**. The API gravity at the end of the experiment for run 2 and run 3 is about 3 points more than that of run 1. Also, the upgrading effects were compared on a plot of viscosities of produced oil measured at 60°C against time as shown in **Fig. 4.42**.

The runs with tetralin and catalysts produced higher average combustion temperatures. Average combustion temperature increased by 17°C for the tetralin-nickel (501°C) when compared to control run (484.1°C). Similarly, average combustion temperatures increased by 8°C for tetralin-iron run (492.1°C) when compared to the control run. This may be because of the hydrogenating effect of the tetralin on the long hydrocarbon chains of the heavy oil. **Table 4.2** shows a summary of results for the four experimental runs carried out during this research.

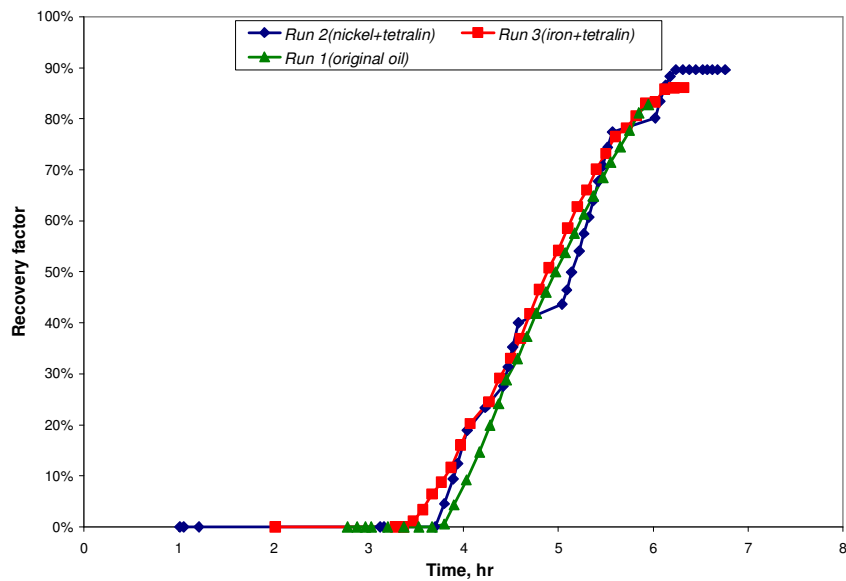


Fig. 4.40—Upgrading effect of catalyst during in situ combustion process shown through comparison of recovery factor.

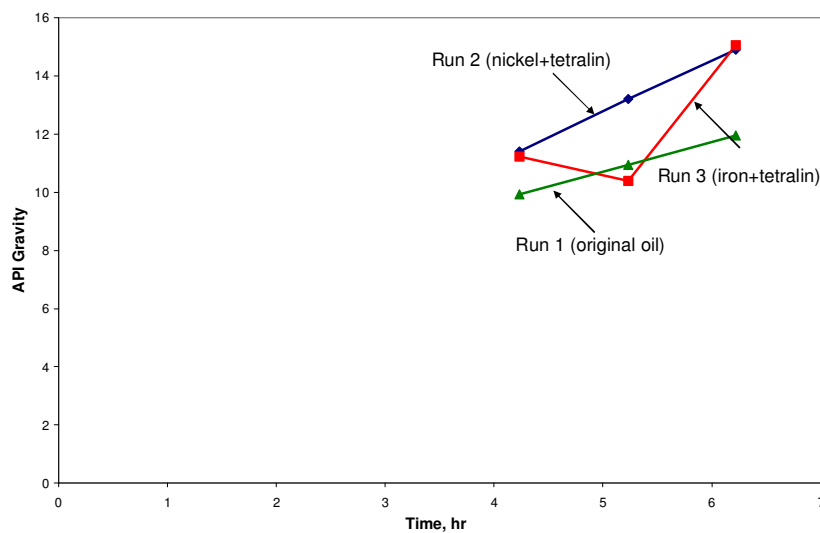


Fig. 4.41—Upgrading effect of catalyst during in situ combustion process shown through comparison of API gravity at end of combustion.

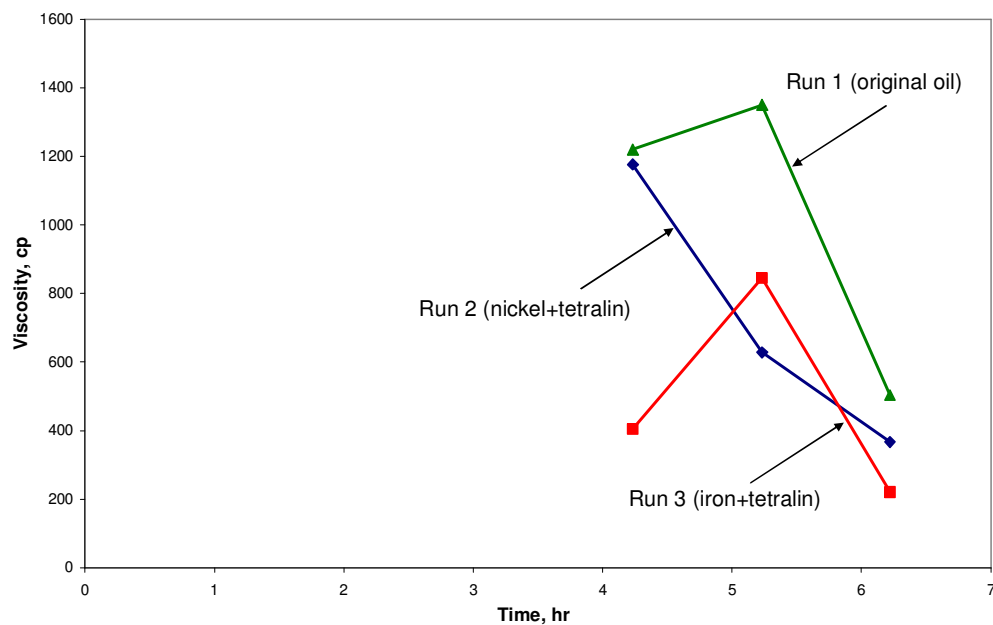


Fig. 4.42— Upgrading effect of catalyst during in situ combustion process showing comparison of viscosity of produced oil at end of combustion.

Table 4.2—Summary of results for experimental runs

	RUN 1 (Mexico heavy oil)	RUN 2 (Mexico heavy oil + tetralin + nickel)	RUN 3 (Mexico oil + tetralin + iron)	RUN 4 (Texas intermediate oil)
<i>m-ratio</i>	0.27	0.25	0.25	0.21
Apparent H-C ratio	3.10	2.42	1.70	1.36
Average combustion temperature (°C)	484	501	492	520
Combustion front velocity (ft/hr)	0.50	0.43	0.46	0.59
Start of oil production (hrs)	3.85	3.80	3.37	4.00
Oil recovery (%)	83	90	86	67
API gravity at end of combustion run	11.90	14.90	15.00	28.10
Viscosity at end of combustion run (cp)	504	367	221	

5 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Summary

The main thrust of my research was to evaluate experimentally the possibility of upgrading and improving recovery of a heavy oil from Mexico (10.2°API) by in situ combustion using tetralin and organo-metallic catalysts. We also determined the applicability of in situ combustion to a Texas intermediate oil (22.0°API) while also evaluating the upgrading effects of in situ combustion on intermediate oils.

Four successful in situ combustion runs were performed with a heavy oil from Mexico and an intermediate Texas oil. For the heavy oil run, a control run (run no. 1) was performed without the addition of tetralin (hydrogen donor) or catalysts (for this study, nickel and iron). For run no. 2 and run no. 3, heavy oil was premixed with tetralin (3% concentration by oil weight) and catalysts (500 ppm). During the experimental runs, the following conditions were kept constant: the air injection rate (3 SL/min) and combustion tube outlet pressure (300 psig).

5.2 Conclusions

The following conclusions were reached from the experiments performed for the heavy oil from Mexico

1. The *m*-ratio was practically the same in the combustion runs with tetralin and catalysts. However, the apparent hydrogen/carbon ratio did not appear to show oil upgrading effect as apparent hydrogen ratio decreased slightly from 3.1 (run 1) to 1.7 – 2.42 for the runs with tetralin and catalysts.

2. Average combustion temperature increased by 17°C for the tetralin-nickel run no. 2 (501°C) when compared to control run no. 1(484°C). Similarly, average combustion temperature increased by 8°C for tetralin-iron run no. 2 (492.1°C) when compared to the control run. This may be because of the hydrogenating effect of the tetralin on the long hydrocarbon chains of the heavy oil.
3. Compared to control run no. 1, oil recovery increased in the tetralin-nickel run no. 2 by 7 points (from 83% to 90% OOIP). In case of iron-nickel run no. 3, recovery increased by 3 points (from 83% to 86% OOIP). The higher recoveries obtained from runs nos. 2 and 3 indicate that the addition of tetralin and metallic catalysts appear to be an attractive method of improving the in situ combustion process.
4. API gravity of produced oil measured at 60°C increased in tetralin-nickel run no. 2 (14.9°API) and tetralin-iron run no. 3 (15.0°API) compared to base run no. 1 (11.9°API). These runs clearly indicate in situ oil upgrading by the addition of tetralin and these metallic catalysts.
5. Produced oil viscosity measured at 60°C in run no. 2 (367cp) and run no.3 (221cp) recorded a drop when compared to viscosity measured for run no. 1 (504 cp). This clear decrease is most likely caused by the hydrogenation of heavy oil by tetralin.
6. The time for the start of oil production decreased from 3.85 hrs (run 1) to 3.78 hrs (run 2) and 3.37 hrs (run 3). This may be due to the reduced oil viscosity during the period of the combustion therefore increasing the flow of oil.
7. For the intermediate Texas oil run (run no. 4), the high average temperature of combustion (520°C) indicated that in situ combustion may be applicable to reservoirs of similar characteristics to the Texas oil reservoir. Also, the produced oil gravity

increased by 6 points (compared to the original oil) showing the upgrading effects of in situ combustion on intermediate oils.

5.3 Recommendations

1. To best simulate real field conditions, the effect of reservoir heterogeneities on the in situ combustion process should be studied alongside the effect of tetralin and catalysts.
2. Further research is necessary to establish a better relationship between catalyst type and oil upgrading. This relationship can further be understood by the use of different catalysts.
3. Carrying out an evaluation of the kinetics of the metallic catalysts to be utilized prior to the combustion runs will give a qualitative idea of the effectiveness of the catalysts.

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APPENDIX

Table A1— Oil and water production table for run no. 1 (control run)

Time(hrs)	Volume of oil(ml)	Volume of water(ml)	Cumulative oil volume (ml)	% Oil Recovery	Cumulative water volume (ml)
2.8	0	7	0	0%	7
2.9	0	15	0	0%	22
3.0	0	8	0	0%	30
3.0	0	1	0	0%	31
3.2	0	20	0	0%	51
3.4	0	17	0	0%	68
3.5	0	8	0	0%	76
3.7	0	33	0	0%	109
3.8	3	13	3	1%	122
3.9	20	8	23	4%	130
4.0	26	6	49	9%	136
4.2	29	4	78	15%	140
4.3	28	4	106	20%	144
4.4	22	5	128	24%	149
4.5	25	3	153	29%	152
4.6	22	5	175	33%	157
4.7	23	4	198	37%	161
4.8	24	2	222	42%	163
4.9	22	5	244	46%	168
5.0	21	0	265	50%	168
5.1	20	0	285	54%	168
5.2	20	0	305	58%	168
5.3	20	0	325	61%	168
5.4	19	0	344	65%	168
5.5	19	1	363	68%	169
5.6	16	2	379	71%	171
5.7	16	0	395	75%	171
5.8	17	0	412	78%	171
5.9	18	0	430	81%	171
6.0	9	0	439	83%	171

Table A2— Produced gas composition for run no. 1 (control run)

Time(hrs)	CO2 (%)	O2 (%)	N2 (%)	CO (%)
0.7	11.64	0.75	82.38	4.35
1.0	10.66	0.79	82.52	4.20
1.4	9.67	0.84	82.65	4.05
2.3	10.44	0.34	82.51	4.01
2.6	10.41	0.33	82.54	3.00
2.9	10.00	0.28	83.10	3.83
3.3	9.42	0.81	83.54	3.52
3.6	8.68	1.73	83.59	3.31
4.1	8.42	1.91	83.68	3.28
4.4	8.56	1.79	83.55	3.25
4.8	8.57	2.00	83.06	3.24
5.1	8.46	1.82	83.35	3.23
5.4	8.81	1.82	82.96	3.18
5.8	8.50	1.36	83.68	3.23

Table B1— Oil and water production table for run no. 2 (tetralin + nickel)

Time (hrs)	Volume of oil (ml)	Volume of water (ml)	Cumulative oil volume (ml)	% Oil recovery	Cumulative water volume (ml)
1.0	0	3	0	0%	3
1.1	0	3	0	0%	6
1.2	0	3	0	0%	9
3.1	0	30	0	0%	39
3.2	0	14	0	0%	53
3.7	0	19	0	0%	72
3.8	23	38	23	5%	110
3.9	24	16	47	9%	126
3.9	15	13	62	12%	139
4.0	33	0	95	19%	139
4.2	22	0	117	23%	139
4.4	21	0	138	28%	139
4.5	19	0	157	31%	139
4.5	19	0	176	35%	139
4.6	24	0	200	40%	139
5.0	18	0	218	44%	139
5.1	14	0	232	46%	139
5.1	17	0	249	50%	139
5.2	21	0	270	54%	139
5.3	17	0	287	58%	139
5.3	16	0	303	61%	139
5.4	16	0	319	64%	139
5.4	19	0	338	68%	139
5.5	15	0	353	71%	139
5.5	18	0	371	74%	139
5.6	15	0	386	77%	139
6.0	14	0	400	80%	139
6.1	16	0	416	83%	139
6.1	16	0	432	87%	139
6.2	9	0	440	88%	139
6.2	7	0	447	90%	139
6.3	0	0	447	90%	139

Table B1. Continued

Time(hrs)	Volume of oil (ml)	Volume of water (ml)	Cumulative oil volume (ml)	% Oil recovery	Cumulative water volume (ml)
6.3	0	0	447	90%	139
6.4	0	0	447	90%	139
6.5	0	0	447	90%	139
6.5	0	0	447	90%	139
6.6	0	0	447	90%	139
6.6	0	0	447	90%	139
6.7	0	0	447	90%	139
6.8	0	0	447	90%	139

Table B2— Produced gas composition for run no. 2 (tetralin + nickel)

Time(hrs)	N2 (%)	CO2 (%)	O2 (%)	CO (%)
0.6	93.05	2.42	0.18	1.26
0.8	87.27	6.90	0.93	3.71
1.0	81.95	11.09	1.06	3.82
1.1	84.81	8.64	2.24	3.84
1.3	82.09	11.02	0.47	3.92
1.5	81.10	11.56	1.54	3.56
1.6	80.87	11.39	1.01	3.77
1.8	80.88	11.79	0.51	3.97
2.0	81.06	10.49	0.69	3.88
2.1	81.51	13.17	1.30	3.86
2.3	80.72	11.83	0.31	3.88
2.5	80.70	10.70	0.71	3.76
2.8	81.04	11.51	0.54	3.74
3.0	81.06	11.55	0.24	3.77
3.1	81.00	11.28	0.42	3.69
3.3	80.83	11.50	0.19	3.69
3.5	81.32	11.04	0.32	3.58
3.6	81.38	11.16	0.00	3.69
3.8	81.25	11.43	0.00	3.66
4.0	81.66	12.26	0.00	3.65
4.1	81.16	10.71	0.15	3.65
4.5	82.22	12.26	0.85	3.55
4.6	81.27	10.50	0.19	3.51
4.8	81.41	10.85	0.19	3.51
5.0	81.28	10.61	0.14	3.49
5.1	81.37	10.52	0.14	3.43
5.3	81.20	10.78	0.00	3.38
5.5	81.47	10.49	0.24	3.36
5.6	81.27	10.34	0.28	3.33
5.8	81.64	10.23	0.26	3.34
6.0	81.50	10.33	0.44	3.28

Table C1— Oil and water production table for run no. 3 (tetralin + iron)

Time(hrs)	Volume of oil (ml)	Volume of water (ml)	Cumulative oil volume (ml)	% Oil recovery	Cumulative water volume (ml)
2.0	0	13	0	0%	13
3.3	0	13	0	0%	26
3.4	0	16	0	0%	42
3.5	7	3	7	1%	45
3.6	13	5	20	3%	50
3.7	18	7	38	6%	57
3.8	14	7	52	9%	64
3.9	17	4	69	12%	68
4.0	26	0	95	16%	68
4.1	25	0	120	20%	68
4.3	25	0	145	25%	68
4.4	27	0	172	29%	68
4.5	23	0	195	33%	68
4.6	23	0	218	37%	68
4.7	29	0	247	42%	68
4.8	28	0	275	47%	68
4.9	25	0	300	51%	68
5.0	20	0	320	54%	68
5.1	26	0	346	59%	68
5.2	25	0	371	63%	68
5.3	19	0	390	66%	68
5.4	24	1	414	70%	69
5.5	18	0	432	73%	69
5.6	20	0	452	77%	69
5.7	10	0	462	78%	69
5.8	14	0	476	81%	69
5.9	15	0	491	83%	69
6.0	1	3	492	83%	72
6.1	15	1	507	86%	73
6.2	2	3	508	86%	75
6.3	1	1	509	86%	76

Table C2— Produced gas composition for run no. 3 (tetralin + iron)

Time(hrs)	N2 (%)	CO2 (%)	O2 (%)	CO (%)
1.0	81.98	13.07	0.75	4.31
1.3	81.88	12.96	0.75	4.42
1.5	81.79	13.30	0.37	4.55
1.8	81.86	13.24	0.36	4.56
2.3	81.80	13.29	0.26	4.57
2.5	82.19	12.12	1.67	4.12
2.8	82.54	12.23	1.16	4.13
3.0	82.78	12.32	0.70	4.24
3.3	82.66	11.93	1.23	4.07
3.5	82.88	11.35	1.97	3.81
4.3	83.22	11.33	1.52	3.79
4.6	83.09	11.38	1.62	3.82
4.9	82.87	11.63	1.46	3.89
5.1	82.84	11.64	1.34	3.71
5.4	83.13	11.34	1.65	3.79
5.6	82.86	11.25	1.80	3.84
5.9	82.72	11.88	1.27	3.86
6.1	82.78	12.26	0.91	3.88
6.4	81.72	12.08	1.17	3.81

Table D1— Oil and water production table for run no. 4 (intermediate oil)

Time (hrs)	Volume of oil (ml)	Volume of water (ml)	Cumulative volume of oil (ml)	% Oil recovery	Cumulative volume of water (ml)
4.0	0	3	0	0%	3
4.0	15	2	15	3%	5
4.1	14	1	29	5%	5
4.2	14	1	43	7%	6
4.3	15	1	57	10%	7
4.4	10	0	67	12%	7
4.5	10	0	77	13%	7
4.6	10	0	86	15%	7
4.7	8	0	94	16%	7
4.8	7	0	101	17%	7
4.9	12	0	113	19%	7
5.0	8	0	120	21%	7
5.1	9	0	129	22%	7
5.2	11	0	140	24%	7
5.3	9	0	148	26%	7
5.4	11	0	159	27%	7
5.5	9	0	168	29%	7
5.6	10	0	178	31%	7
5.7	11	1	189	33%	7
5.8	9	1	197	34%	8
5.9	12	0	209	36%	8
6.0	14	0	223	38%	8
6.1	25	0	247	43%	8
6.2	6	0	253	44%	8
6.3	9	0	262	45%	8
6.4	4	0	266	46%	8
6.5	15	0	281	48%	8
6.6	15	0	296	51%	8
6.7	18	0	313	54%	8
6.8	12	0	325	56%	8
6.9	15	0	340	59%	8
7.0	12	0	352	61%	8
7.1	11	0	363	63%	8
7.2	13	0	376	65%	8
7.3	3	0	379	65%	8
7.4	10	0	389	67%	8

Table D2— Produced gas composition for run no. 4 (tetralin + iron)

Time(hrs)	S/N	CO2 (%)	O2 (%)	N2 (%)	CO (%)
1.0	3	10.72	2.67	81.57	3.01
1.1	4	11.88	1.92	81.12	3.12
1.3	5	12.74	1.39	80.93	3.33
1.5	6	13.11	1.23	80.43	3.55
1.6	7	12.67	1.18	80.74	3.52
1.8	8	12.70	1.59	80.47	3.33
2.0	9	14.00	0.55	80.38	3.52
2.1	10	14.11	0.46	80.38	3.54
2.3	11	13.86	0.36	80.70	3.48
2.5	12	13.52	0.23	80.49	4.01
2.6	13	13.78	0.67	81.57	3.96
3.0	14	14.38	0.49	79.65	3.64
3.1	15	13.71	0.61	80.12	3.71
3.3	16	13.77	0.18	80.58	3.55
3.5	17	13.71	1.47	81.34	3.48
3.6	18	14.19	0.15	80.24	3.49
3.8	19	14.29	0.00	80.05	3.51
4.0	20	13.50	0.70	80.43	3.18
4.1	21	13.44	0.41	80.49	3.53
4.5	22	14.24	0.10	80.10	3.47
4.6	23	13.76	0.10	80.04	3.96
4.8	24	13.53	0.00	80.08	4.25
5.0	25	13.90	0.00	79.89	3.66
5.1	26	14.55	0.11	80.07	3.21
5.3	27	13.80	0.20	80.78	3.21
5.5	28	14.51	0.23	79.53	3.37
5.6	29	14.17	0.00	79.60	3.56

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