

STEAM PYROLYSIS OF TOSCO SHALE OIL
FOR PRODUCTION OF CHEMICAL INTERMEDIATES

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INTRODUCTION

The recent national concern for developing new sources of energy has increased interest in creating ways to utilize the vast reserves of oil shale in the U.S. This attention is evidenced in the numerous commercial projects being undertaken for the production of synthetic fuels from oil shale (1). Research and development of synthetic fuels from oil shale has been directed toward processing schemes involving retorting followed by a combination of coking, hydrostabilization, hydrodenitrogenation, reforming, and cracking (2).

Typically, crude shale oil has a high content of organic nitrogen (2% by weight) as reported by Sladek (3) and Atwood (4) and comprehensively characterized by Poulson, et al. (5) and Cook (6). Since nitrogen is a poison for current refinery catalysts, existing refineries would not be able to cope with the high nitrogen content of raw shale oil if it were a substantial part of the refinery feed (2,7). Frost, et al. (7) reports that the National Petroleum Council has suggested that crude shale oil be upgraded at the retorting site. The Energy Research and Development Administration in Laramie has developed a method for refining shale oil that involves the upgrading proposed by the National Petroleum Council (8). The upgrading would require severe prerefining steps. Thus, any alternative use of shale oil that does not require prerefining may be both practical and economical.

An alternative use of shale oil is as a feedstock for production of chemical intermediates such as ethylene, propylene, benzene, toluene, and xylene. Steam pyrolysis of hydrocarbon feedstocks is the most extensively used method for production of petrochemical intermediates (9). Since steam pyrolysis is not a catalytic process, it may not require severe prerefining of the feedstock. It therefore becomes an attractive alternative.

Previous studies of the utilization of shale oil as a steam pyrolysis feedstock have been undertaken by the U.S. Bureau of Mines (10) and the Institute of Gas Technology (11) with significant results. Chambers and Potter (12) report maximization of ethylene should be the objective of steam pyrolysis.

The role of ethylene as a chemical building block in the petrochemical industry is great and will not be further discussed here. Traditionally, most ethylene has been produced by cracking ethane and propane due to the high product yields possible. However, recently the availability of ethane and propane for feedstocks has not kept up with the demand. The continuity of feedstock supply is almost more important than feedstock price (13). Recently naphtha and heavier feedstocks have been used as alternative feedstocks for ethylene production.

"Developmental studies of crude oil pyrolysis indicate that ethylene and other olefins can be produced at lower cost and higher return on investment than by conventional naphtha pyrolysis." (14)

Thus, crude shale oil may be utilized as an economical, readily available feedstock for ethylene production.

An overall research program has been developed to study the utilization of shale oil produced from several retorting processes as a feedstock for steam pyrolysis. The effects of feed composition, operating variables, and nitrogen

level on product distribution will be studied. The objective of this first stage of the overall research program is to develop a steam pyrolysis unit to study the utilization of shale oil produced from the TOSCO II retorting process as a feedstock for steam pyrolysis with a major goal of obtaining maximum ethylene production.

EXPERIMENTAL BASES

Previous Work

Pyrolysis has been established as an effective process for producing chemical intermediates. Processes have been proposed and/or developed for cracking crude (13,14,15,16,17), vacuum gas oil (18), and vacuum residuum (19). The previous significant experimental work with shale oil has been done by the Laramie Energy Research Center of the Energy Research and Development Administration (10,20) and the Institute of Gas Technology (11).

One series of tests by the Laramie Center involved the retorting of pulverized oil shale, entrained in steam or other gaseous media, in a vertical tube high temperature retort. In another series, shale oil from a conventional retort was pyrolyzed for comparison purposes. The latter series is the one relevant to this study. The results show a significant conversion to the chemical intermediates of interest; however, all runs were made below 1200°F, which is below the temperature interval of interest in this study.

The studies made by the Institute of Gas Technology involved the steam pyrolysis of a crude shale oil in a continuous flow vertical tube reactor. The experimental runs were made at higher temperature than the Laramie tests. The shale oil studied was produced from Green River formation shale by the Bureau of Mines gas combustion and the Union Oil Co. processes. The experiments were run for reaction times over the 1- to 4.5-second range at 1400, 1470, and 1550°F for gasification at atmospheric pressure, at partial pressures of the product gas from 0.64 to 0.76 atm. Thus, while the temperature range is sufficiently high, the reaction times are relatively high. The results obtained by IGT will provide a basis for comparison.

Reaction Variables

Feed composition: The ultimate yields of chemical intermediate products is greatly dependent on the composition of the feedstock. Numerous studies have been conducted to determine the yields from both pure compounds and commercial feedstocks. The ease of conversion of various feedstocks to ethylene has been summarized by Zdonik, et al. (18) and Vanderkooi (21). The feedstocks in order of decreasing convertability are:

1. normal-Paraffins
2. iso-Paraffins
3. naphthenes
4. olefins
5. aromatics

Feeds and corresponding products of interest are summarized below:

<u>Feed</u>	<u>Product</u>	<u>Reference</u>
Paraffin	Light olefins	18,21
Light Olefins	Benzene + Toluene other light olefins	22,23
Naphthenes	Light olefins aromatics	18
Aromatics	Unconverted	18,21

Generally, yields of olefinic and aromatic products decrease as the weight of the feedstock increases. Additionally, the lighter olefins may undergo secondary reactions with each other to condense into monoaromatics (22,23). Thus, feedstocks having different paraffin-olefin-naphthene-aromatic (PONA) compositions and different weights will produce different product compositions.

The shale oil to be pyrolyzed in this study is from a TOSCO II process retort with properties (24):

Gravity	21 API
Sulfur	0.7 wt %
Nitrogen	1.9 wt %
Molecular Weight	300

Distillation curves for the TOSCO oil and crude shale oils from the gas combustion retorting process and the Union Oil retorting process (the oils used by the Institute of Gas Technology) are readily available (25).

Temperature: Chambers and Potter (12) report that cracking reactions at highest temperature gave maximum ethylene yields. As temperature is increased, hydrogen, methane, and ethylene yields go up, propanes, butanes, and pentanes go up then down, and hexanes and non-aromatics go down (21). The Institute of Gas Technology (11) conducted their pyrolysis tests between 1400 and 1550°F. Dow Chemical (21) operates between 1382 and 1562°F.

Time: For maximum yields of light olefins, low hydrocarbon residence time is essential (26). The previous studies have been made with residence time ranges of 0.5-1.5 seconds (21) and 1.0-4.5 seconds (11). The importance of low residence times is explained by Kamptner (17):

"The chronological course of the reaction influences the occurrence of disturbing secondary reactions which are generally noticeable in a reduction in the yield of valuable primary cracked products."

The residence time is based on the reactor void volume, the volume of steam flow at atmospheric pressure and reaction temperature, and the ideal-gas volume of 300-molecular-weight oil at atmospheric pressure and reaction temperature.

Steam-oil ratio: In steam pyrolysis, the steam acts as a diluent to prevent excessive coke formation, as an oil preheat heat source, and as a carrier medium. In the temperature range of interest the steam does not participate in the reactions. Studies have been made with steam-hydrocarbon mass ratios of 0.2-0.8 (21) and 0.5-1.0 (26) for feedstocks in the range light naphtha to heavy gas oil.

Pyrolysis severity factor: Numerous severity factors have been developed and/or utilized for correlating pyrolysis results (11,12,21,26,27,28). The most common severity factor is that used by the Institute of Gas Technology which takes the form:

$$S = T\theta^{0.06} \quad 1)$$

where S is pyrolysis severity factor

T is reaction temperature, F

θ is residence time, sec.

The results of this study are correlated with the IGT severity factor with an additional factor to account for the effect of steam-hydrocarbon ratio.

APPARATUS AND PROCEDURE

The continuous flow reactor used in this study (Figure 1) consisted of a 12-inch externally heated section of 1-inch schedule-40 stainless steel pipe. The

reactor was packed with 1/2-inch porcelain balls. Chromel-alumel thermocouples connected to a temperature recorder monitored the temperature within the reaction zone. The heat was supplied by a Linberg single-zone tube furnace. The current to the heated zone was controlled with a Lindberg single-zone control unit that responded to a Platinel II thermocouple in the middle of the heated zone.

Below the reactor was a heavy oil separator in which the steam and heavy oil was condensed and collected. The remaining vapor then passed through a series of water and ice-water condensers and a filter to remove any remaining condensables.

The oil was fed to the reactor with an adjustable-stroke positive-displacement pump. Distilled water was fed through a boiler and superheater and mixed with the oil at the entrance of the reactor. Liquid feed rates were determined by direct measurement of volume flowed during the reaction period.

Gaseous products flow rates were measured with a wet-test meter. Gaseous product compositions were determined by conventional gas chromatography. Solid carbon deposition in the reactor was determined by measuring the weight gain of the reactor packing.

RESULTS

A series of experimental runs were made to determine the relationship between the reaction variables and product yields. A detailed compilation of the reaction conditions and corresponding product analyses is available elsewhere (29). The effects of the reaction variables are discussed in the following sections.

Temperature

Tests for temperature effects were made at temperatures of 1300, 1450, and 1600°F for 0.8 sec residence time and 0.8 steam-hydrocarbon ratio. In Figure 2 the volumetric gaseous product yields are plotted as a function of reaction temperature.

Increasing temperature rapidly increases both the weight percent of the feed converted to gaseous products and the total volume of gaseous products. Gaseous product yields ranged from 3.96 standard cubic feet per pound and 31.46 weight percent converted at 1300°F to 9.23 standard cubic feet per pound and 56.68 weight percent converted at 1600°F.

As can be seen in Figure 2, increasing temperature significantly increases the yields of hydrogen, methane, and ethylene. Higher temperatures promote extensive additional cracking of the vaporized oil and thus the increased production of the lighter gaseous products. Ethylene production increased from 1.17 standard cubic feet per pound at 1300°F to 3.27 standard cubic feet per pound at 1600°F. Corresponding increases of methane from 0.86 to 3.93 and hydrogen from 0.18 to 0.49 were obtained. Propylene production increased from 0.71 standard cubic feet per pound at 1300°F to 0.97 at 1450°F and then decreased to 0.52 at 1600°F due to further cracking to lighter products.

Residence Time

The effect of residence time within the reactor was investigated at times of 0.4, 0.8, and 1.2 sec for 1450°F temperature and 0.8 steam-hydrocarbon ratio. The volumetric gaseous product yields are plotted as a function of residence time in Figure 2.

For the low residence times investigated a great variation in product yields and compositions was not expected as shown in Figure 2. As residence time is increased from 0.4 to 1.2 sec the weight percent converted to gaseous product

increases from 50.06 to 54.44, and the volumetric gaseous product yields increase from 6.78 to 7.84 standard cubic feet per pound. As residence time was increased from 0.4 to 1.2 sec, hydrogen yields increased from 0.31 to 0.45 standard cubic feet per pound, methane yields increased from 1.92 to 2.46, and ethylene yields increased from 2.44 to 2.78. Propylene yields remained essentially constant at 1.0 standard cubic feet per pound.

Steam-hydrocarbon Ratio

Experimental runs were made to investigate the effect of steam-hydrocarbon ratio on product yields and compositions at ratios of 0.4, 0.8, and 1.2 for 1450°F temperature. The volumetric gaseous product yields are plotted as a function of steam-hydrocarbon ratio in Figure 2.

As shown in Figure 2 the effect of increasing the steam-hydrocarbon ratio is similar to increasing the residence time. As the ratio is increased from 0.4 to 1.2, the weight percent conversion to gaseous products increases from 49.31 to 55.63, and the volumetric gaseous product yields increase from 7.02 to 7.88 standard cubic feet per pound.

Although increasing the ratio increases cracking, the cracking tends more toward production of ethylene rather than methane. As the ratio was increased from 0.4 to 1.2, hydrogen yields increased from 0.34 to 0.48 standard cubic feet per pound and ethylene increased from 2.41 to 2.87. Methane production remained nearly constant between 2.2 and 2.3 standard cubic feet per pound. Propylene yields remained essentially constant at 1.0 standard cubic feet per pound.

Pyrolysis Severity Factor

The pyrolysis severity factor combines the effects of all the reaction variables on product compositions and yields into one variable. The IGT severity factor (11) will be used with an additional factor to account for the effect of steam-hydrocarbon ratio. The relation that will be used for correlation is:

$$S = T\theta^{0.06} \text{ ratio}^{0.05} \quad 2)$$

where ratio is the steam-hydrocarbon mass ratio.

Figure 3 shows the effect of pyrolysis severity factor on volumetric gaseous product yields. Greater severity of operation yields greater volumes of paraffins (mainly methane) and light olefins.

Figure 4 shows the gas composition in mole percent as a function of the pyrolysis severity factor. Greater operation severity results in increased hydrogen and methane contents and decreased contents of higher paraffins and olefins. Except for the low temperature run, the ethylene content was nearly constant in the range 34.37-36.39 mole percent.

The effect of severity on light olefin production is shown in Figure 5. Greater severity of operation results in the following trends: ethylene production first increases rapidly and then tapers off to a steady rise. If severity were increased beyond the range of this study then an eventual decrease in ethylene production can be expected via secondary reactions as predicted by Kamptner (17) and obtained by IGT (11). The maximum yield of ethylene obtained was 3.3 standard cubic feet per pound which corresponds to 24.2 weight percent of the feed. Propylene production gradually increases, then gradually decreases due to further cracking via secondary reactions. Propylene yield peaked at 1.0 standard cubic feet per pound or 10.8 weight percent of the feed. Combining both ethylene and propylene yields into a total light olefin yield results in a rapid initial increase which levels off to a constant production rate and then begins to decrease

at high severity. The maximum total light olefin yield was 3.8 standard cubic feet per pound and 31.8 weight percent of feed.

Figure 6 shows the effect of severity on solid products. Carbon deposits increase approximately linearly with pyrolysis severity.

Comparison with IGT

Figure 7 compares the results of a study of crude shale oil pyrolysis by the Institute of Gas Technology with the experimental results of this study. Total gaseous product volumetric yields and ethylene yields are compared. The IGT tests were made on crude shale oil from the gas combustion retorting process and the Union Oil retorting process, while crude shale oil from a TOSCO II process retort was used in this study. The TOSCO oil has a much greater quantity of light ends than the other two oils. Thus a higher total gas and ethylene production would be expected. Figure 7 shows the expected higher production. The total volume of gaseous products from the TOSCO oil is consistently higher than the total volume from the IGT tests for constant reaction severity. Significantly greater yields of ethylene were also obtained at constant reaction severity.

The comparison of the two studies is limited to a qualitative comparison only. The uncertainty is caused by different procedures for calculating residence time. Reaction times for IGT's tests were calculated on the basis of the final product rate, the "average indicated" reaction temperature, reactor pressure, and the reactor volume. However, the method of determining the "average indicated" reaction temperature was not reported. The residence times for this study were calculated on the basis of the reactor void volume, the volume of steam flowed at atmospheric pressure and reaction temperature, and the ideal gas volume of 300-molecular-weight oil at atmospheric pressure and reaction temperature. Additionally, temperature profiles were measured along the length of the reactor. The measurements showed that the temperatures at the exit and entrance of the reactor were considerably lower than the reaction temperature.

CONCLUSIONS

The results of the study of steam pyrolysis characteristics of a TOSCO II shale oil were reasonably successful. Up to 24 weight percent of the feed was converted to ethylene, and up to 6 weight percent was converted to propylene. The results are comparable with reported results and predictions for crude oil, gas oil, and shale oil. For example, Sherwin and Fuchs (30) have predicted yields of 23 weight percent ethylene and 5 weight percent propylene for cracking unrefined shale oil. Additionally, Stork, et al. (13) report expected ethylene yields greater than 20 weight percent for several proposed petrochemical refinery schemes.

Within the ranges studied, an increase in any one of the reaction variables resulted in an increase of severity of operation. The effect of increasing the temperature was extreme, while increasing the residence time or steam-oil ratio had a much smaller effect. A modified form of a commonly used pyrolysis severity factor satisfactorily correlated the experimental results. Increasing the severity of operation resulted in increases in weight percent of feed converted to gaseous and solid products, in total volume of gaseous products, and in volumetric yields of methane and ethylene. The total light olefin yields increased sharply, then leveled off and began to decrease with increasing severity.

The yields obtained from the TOSCO oil were greater in total gas and ethylene than crude shale oil from the gas combustion retort.

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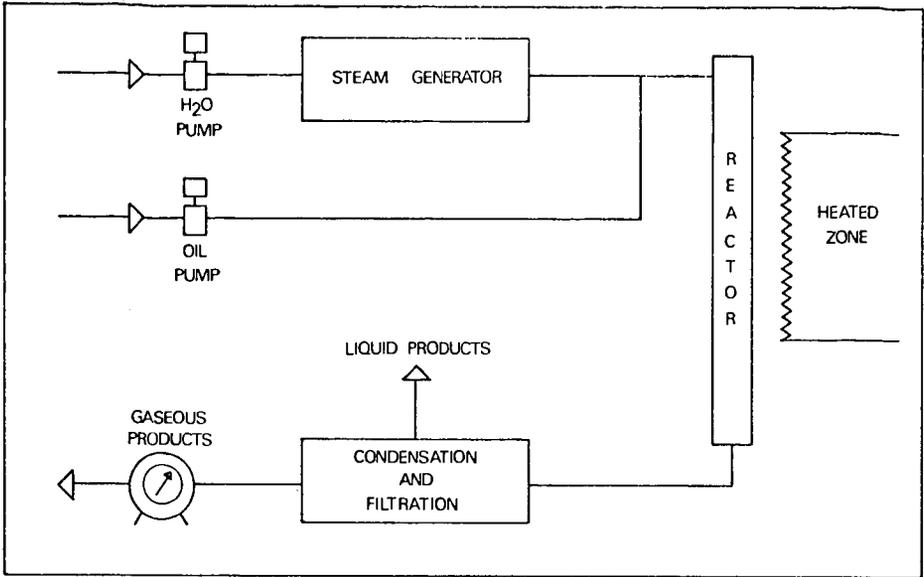


Figure 1. Reactor system

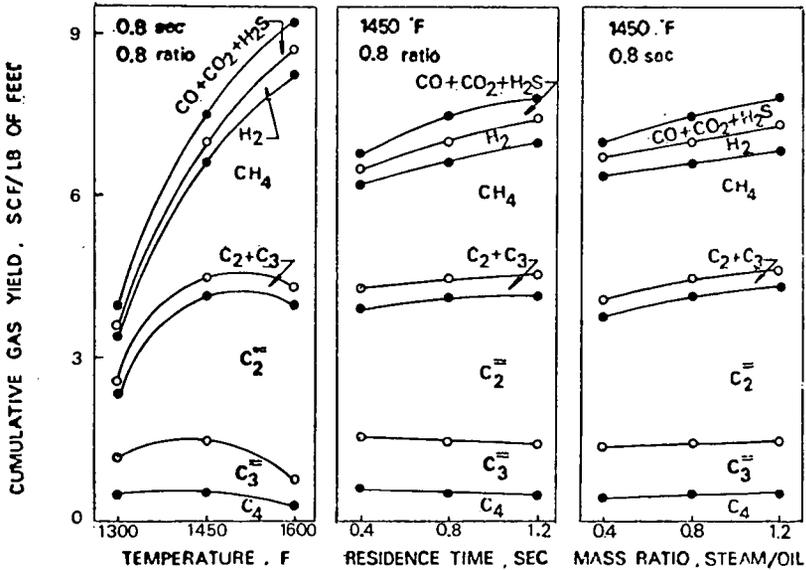


Figure 2. Effect of reaction variables on cumulative gas yields

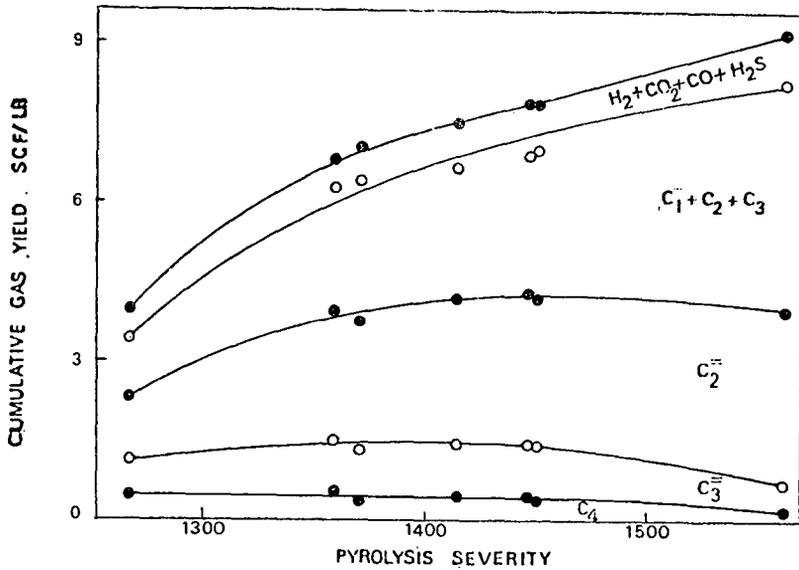


Figure 3. Effect of pyrolysis severity on volumetric gas yields

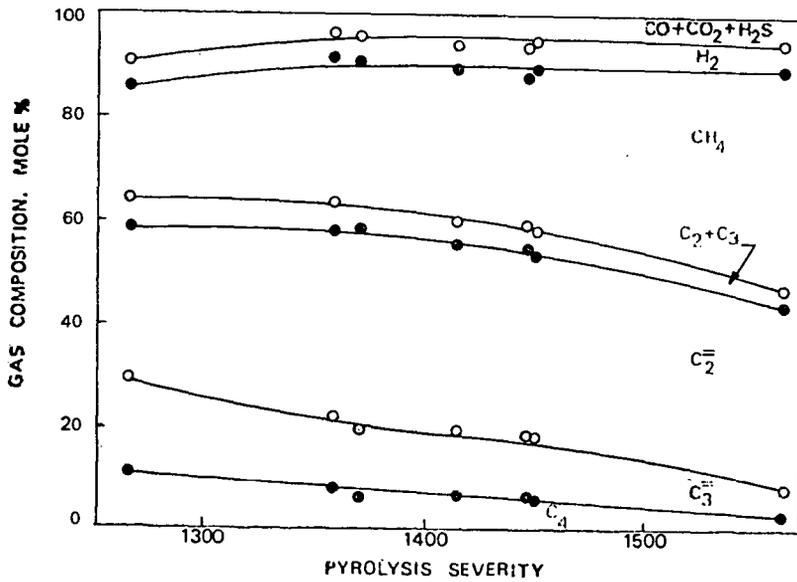


Figure 4. Effect of pyrolysis severity on product gas composition

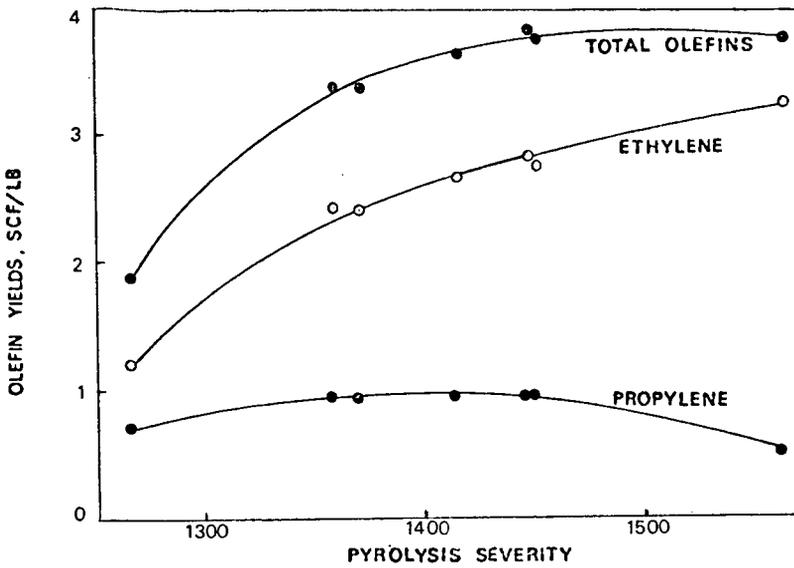


Figure 5. Effect of pyrolysis severity on olefin yields

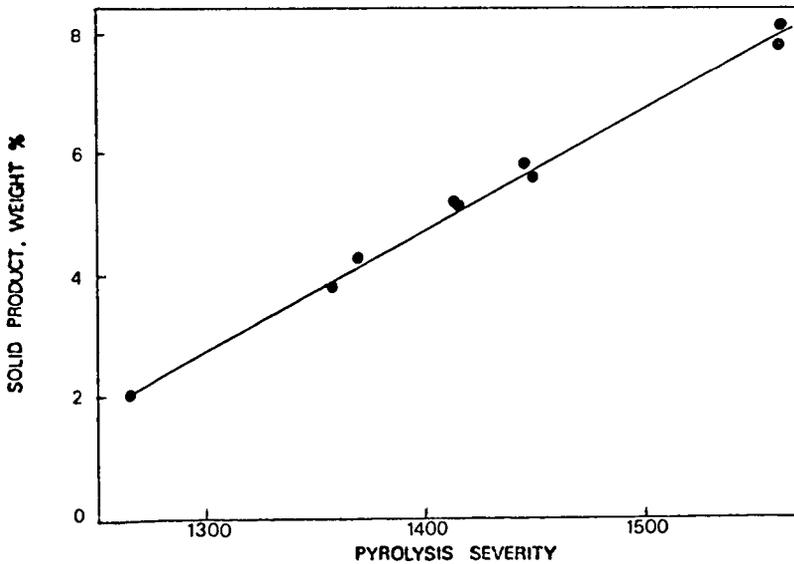


Figure 6. Effect of pyrolysis severity on solid product yields

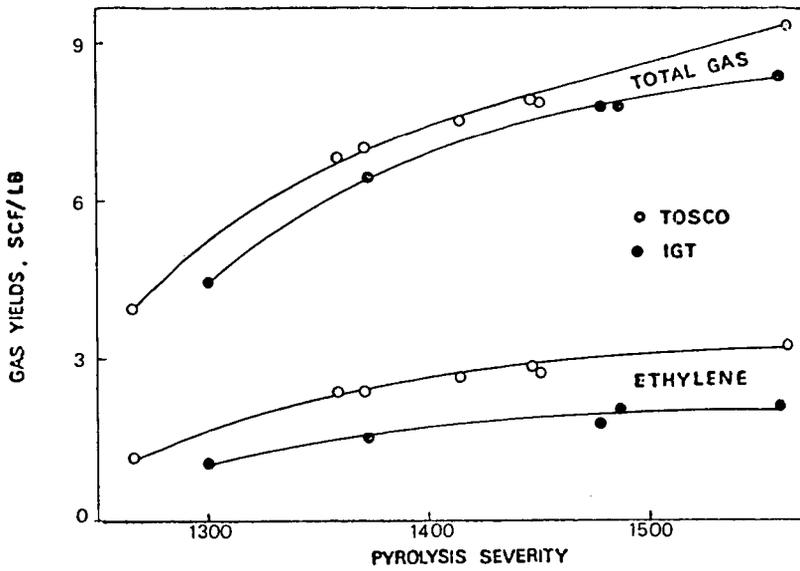


Figure 7. Yield comparisons between TOSCO and IGT oils