

CANMET

**CONVERSION OF POLYETHYLENE TO
TRANSPORTATION FUELS
THROUGH PYROLYSIS AND CATALYTIC
CRACKING**

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EXECUTIVE SUMMARY

A high density polyethylene was thermally cracked in both a closed tubing bomb reactor at 450-500°C and an open system using the same reactor at 480°C. In the closed system, distillate yield increased at a higher temperature which also accelerated the formation of gases and coke. Secondary reactions such as saturation, isomerization, cyclization and aromatization were found at high severity. In contrast, the open system produced less naphtha but more gas oil. Compositionally, the distillates contained more olefins, less saturates and very little aromatics, compared with those from the closed system. Pyrolytic waxy products from polyethylene were catalytically cracked in a fixed bed reactor at 470 and 510°C, respectively. High yields of gasoline of improved quality and liquefied petroleum gas were obtained along with a small amount of low value products such as dry gas, heavy cycle oil and coke.

Keywords: plastic wastes, tertiary recycling, fuels, pyrolysis of polyethylene, catalytic cracking.

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INTRODUCTION

In recent years there has been a worldwide growing concern, especially in industrialized countries, over the disposal of various types of wastes including those originating from plastics. Currently, Canada produces 0.5-1.0 million t/a of plastic wastes of which less than 5% is recovered or recycled. The rest is shipped to garbage dumps at costs up to \$150/t. The increased consumption of plastics in a modern society is inevitable due to their versatile utilities, functional values and the relative small amount of energy required for their production, compared with other materials. This trend, combined with the fact that suitable landfill sites are gradually more difficult to obtain, has prompted researchers to re-focus on plastics recycling technology. In the 1970s, research activities in this area were attributable to the energy crisis. Following the decline in oil prices, most research efforts were reduced or even eliminated. With the new initiatives driven by both environmental concerns and economic factors, different approaches are being taken to make plastics recycling viable and more cost effective. Similar to solid waste management, plastic waste recycling can also be categorized into four modes (1). Primary recycling deals with conversion into products of a nature similar to the original product. Secondary recycling involves conversion into products of different forms for less demanding applications. Tertiary recycling converts wastes into basic chemicals or fuels and is unique to plastics. Quaternary recycling retrieves energy from wastes through combustion. A typical example is the incineration of wastes for power generation. Today, secondary recycling (the cheap way) is a more common practice for many plastic products by grinding, remelting and reforming them into lower value products such as fillers and fibers. Its application is somewhat limited. In Europe, only less than 20% of plastic waste can be handled this way (2). As far as recycling is concerned, plastic wastes after a number of primary and secondary recyclings will eventually have to be treated in the tertiary or quaternary mode. Although burning plastics for energy is a more

mature and established technology, there is strong opposition to incineration since the public is not fully convinced that the value of plastics is best recovered through this source-elimination procedure. Further, siting a new incinerator can be very difficult and faces public sensitivity. In contrast, tertiary recycling of plastic wastes is gaining momentum as petroleum and petrochemical companies begin to realize that this technology can be integrated into their daily operations. Moreover, it will become profitable if a fee of \$150-190 can be charged for processing 1 t of plastic wastes (3 and 4). This is reflected by a number of pilot, demonstration and commercial plants processing various types of plastic wastes in Germany, Japan, USA and elsewhere. Companies such as Amoco, Shell, BP, Chevron, Esso, Veba, RWE and Fuji Recycle, have R&D programs to evaluate this approach (5, 6, 1, 7, 8, 9 and 2). Just recently, it was announced that BASF plans to build a \$175 million commercial recycling plant to convert plastic wastes into a mixture of naphtha, olefins and aromatics (4).

The majority of these R&D programs deals with hydrolysis, methanolysis and amminolysis for condensation polymers (e.g., polyethylene terephthalate and urethane) and hydrogenation, pyrolysis, gasification, liquefaction, hydrocracking, coking and visbreaking for addition polymers (e.g., polyolefins, polystyrene and polyvinyl chloride). Among these, catalytic cracking seems to be overlooked. Therefore, CANMET has conducted a series of batch tests including catalytic cracking and pyrolysis of polyethylene and polystyrene which constitute over 60% of plastic wastes in the USA (10). This study forms part of CANMET's research program for conversion of waste plastics to fuels, petrochemicals, α -olefins (1-alkenes), synthetic lubricants and surfactants. Primary data obtained from this study are presented here.

EXPERIMENTAL**Materials**

The plastics used in this study were high density polyethylene (HDPE) resin pellets (DMDA 200, 1.5 mm diam x 3 mm h) from Union Carbide Corp. and low density polyethylene (LDPE) thin clear films (1 cm²) cut from a large 50 cm x 70 cm polyethylene (PE) bag from Petromont Inc. An Akzo Chemicals equilibrium fluid catalytic cracking (FCC) catalyst, KOB-627, was obtained from Petro-Canada's Oakville refinery.

Characterization of feedstocks and catalyst

Feedstocks were characterized using ASTM and other supplementary methods. Analyses included density (D-1505), elemental carbon, hydrogen and nitrogen by Perkin-Elmer 240, sulphur by X-ray fluorescence (D-4294) using a Gamma Tech Model 100, simulated distillation (D-2887), contents of n-paraffins and α -olefins by capillary GC Perkin-Elmer Sigma 2000.

Prior to characterization, the cracking catalyst was decoked at 590°C for 3 h. Surface characteristics were determined by N₂ adsorption-desorption (Quantachrome Autosorb) and mercury porosimetry (Micromeritics Autopore 9200). Zeolite surface areas and zeolite contents were estimated based on a method reported in the literature (11). Metal contents (V, Ni and Al₂O₃) were determined by ICP. The unit cell dimension of zeolite crystal was measured by X-ray diffraction.

Pyrolysis of pe in a tubing bomb reactor and characterization of cracked products

Most pyrolysis tests were conducted in a tightly sealed (with copper gaskets in place) 100 mL tubing bomb reactor which was fixed to an upright rod. This rod moved up and down vigorously during a run to agitate the reactant (about 20 g of HDPE resin pellets or LDPE thin films in N₂ atmosphere) mixed with steel bearing balls inside the reactor which was immersed in a hot fluidized sand bath. The internal reactor temperature was monitored by a

thermocouple and controlled by the addition of cold sand to the hot fluidized sand bath when overheating occurred. The reactor could be brought to a desired temperature (450-500°C) from the cold state in about 8 min after being immersed in the hot bath. After 10 min at the reaction temperature, the bomb reactor was taken out of the sand bath and cooled by spraying water mists. The final pressure at the reaction temperature ranged from 1.38 to 16.13 MPa (200 to 2340 psi) when PE was decomposed at 450-500°C. The gaseous product from the reactor was collected in a sampling bag for GC analysis and the gas volume was measured by water displacement. The product slurry was scraped out of the reactor and was separated by distillation into naphtha (220°C-), gas oil (220-500°C) and residue (500°C+). The residue was dissolved in tetrahydrofuran (THF) to determine the coke content which was the THF insolubles (THFI). The naphtha was further separated into several compound types (saturates, olefins and monoaromatics) by a high performance liquid chromatograph (HPLC, Deltaprep 500) equipped with a silica gel column. The distillates and their HPLC fractions were analyzed by capillary GC (Perkin-Elmer Sigma 2000) with FID and GC-MS (HP 5890GC + 5770MSD).

A few experiments were performed in an open system using the same tubing bomb reactor. In this case, a stream of nitrogen at 100 mL/min flowed through the reactor before and during the reaction. The desired temperature was reached 10-15 min after the reactor was immersed in the hot bath. The reactor was kept at the reaction temperature for 10 min. Cracked products mixed with N₂ first passed through a cold trap at 0°C where the liquid product was separated. The incondensable product was then collected in a sampling bag. In a high temperature run, a significant portion of the reactant was decomposed before the desired final reaction temperature was reached as evidenced by the accumulation of liquid product in the cold trap. The liquid product ceased to come out prior to the end of the reaction time. After the reaction, cracked products were processed and analyzed like those in the closed system.

Catalytic cracking of feedstocks in a fixed bed reactor and characterization of cracked products

Catalytic cracking of waxes A, B and C obtained from the pyrolyses of LDHP and HDPE was conducted in an automated microactivity test (MAT) system (Zeton Automat IV). The MAT unit was a modified version of ASTM D-3907 equipped with a gas collection system. The reactor was loaded with 4 g catalyst KOB-627. Before and during reaction, the unit was purged with nitrogen at 20 mL/min. The feed was delivered by a constant drive syringe pump through a syringe which was heated at about 60°C. After injection into the reactor, the feed was vaporized in the preheat zone and was cracked in the catalyst bed. The nitrogen purge continued and the run was terminated 30 min after the feed injection. The liquid product was collected in a glass receiver at 0°C (25 min) and 25°C (5 min) and was analyzed for simulated boiling point distribution by GC (D-2887). For selected runs, liquid products were also analyzed separately for PIONA by using (1) Hewlett Packard 5890 GC equipped with HP Ultra-1 capillary column (50 m x 0.2 mm); (2) automated Multi-Dimensional GC (MDGC) composed of Hewlett Packard 5890 Series II GC and Analytical Controls PIONA ChemStation. MDGC was found suitable to analyze olefinic gasolines for hydrocarbon types by carbon number (12). By using a proprietary software, MDGC could also report research octane number (GC RON) and motor octane number (GC MON) based on a correlation between PIONA analyses and ASTM engine test results on FCC gasolines. The gas sample was also analyzed by GC for various components. The coke deposited on the catalyst after cracking was determined in situ by passing a stream of air through the catalyst bed. The exhaust gas passed through a catalytic reactor to convert carbon monoxide into carbon dioxide. The CO₂ generated was measured by an infrared analyzer as well as by a CO₂ absorber. Test severity was adjusted by varying the catalyst/oil (cat/oil) ratio and temperature with constant weight hourly space velocity (WHSV) at 20 h⁻¹. The results reported for each MAT run included conversion, yields of dry gas, liquefied petroleum gas (LPG), gasoline, light cycle oil (LCO), heavy cycle oil (HCO) and coke.

RESULTS AND DISCUSSION

The objective of this study was to assess the processability of PE for conversion into transportation fuels, i.e., gasoline or diesel, through thermal or catalytic cracking. To meet the specifications of transportation fuels, an oil must acquire certain basic properties some of which are the knocking characteristics (reflected by octane numbers) for gasoline and the ignition quality (reflected by cetane number) for diesel fuel. In a refinery, FCC operation produces a significant amount of high octane gasoline composed of olefins, monoaromatics, branched paraffins and naphthenes. It accounts for 30-40 vol.% of the gasoline pool (13). Through alkylation of i-butane and C₃-C₅ olefins, an additional (about 11 %) high octane gasoline can be produced (14). LCO from FCC is a poor diesel fuel because its high aromatics content lowers cetane number and releases carbonaceous particulates in the exhaust gas during combustion. In North America, unless the supply of home heating oil or natural gas is a problem, producing high octane gasoline from vacuum gas oils is the general goal in FCC operation. In contrast, thermal cracking and coking which exclude the use of catalysts and are thus nonselective processes can only produce low octane naphtha consisting of high amounts of straight chain olefins and even diolefins which are gum-forming (15). In addition to process type and operating conditions, feedstock and catalyst properties are important for determining quality and quantity of cracked products.

Feedstock and catalyst properties

Table 1 shows the properties of HDPE, LDPE, and waxes A, B and C. The two types of PE appear to have different physical properties only. Their H/C atomic ratios are almost identical (1.956 for HDPE and 1.964 for LDPE) which are of the approximate magnitude as their monomer's (2.000 for C₂H₄). Wax A was obtained from pyrolysis of LDPE in a closed system at 460°C whereas B and C were from HDPE in an open system at 470 and 480°C,

respectively. Carbon and hydrogen analyses of the waxes are same as those of their parent feeds. As far as boiling range is concerned, wax A is the heaviest, followed by B and C. The open system produced much more α -olefins (wax B) compared with the closed system at a slightly lower temperature (wax A) as olefins formed were swept away from the reactor prior to their further reactions such as saturation, isomerization and aromatization. The higher temperature in the open system also produced more α -olefins as reflected in the analyses of B and C, but the difference is not as great as that between the closed and open systems.

Table 2 shows the property of FCC catalyst KOB-627. This is an octane-enhancing catalyst containing ultra-stable Y type (USY) zeolite which has a smaller unit cell size compared with those containing rare-earth exchanged Y type (REY) zeolites. This is due to the dealumination treatment of USY zeolites (16). Metal analysis indicates that the catalyst was not seriously contaminated by the commercial FCC process. The catalyst is of medium activity based on its zeolite content.

Thermal cracking of HDPE in a closed system

Primary thermal gravimetric study of HDPE indicates that it begins to decompose at about 450°C. Table 3 shows the results of thermal decomposition of HDPE performed at 450-500°C in a closed system. At 450°C, very little gases were produced and the yield of distillate (naphtha + gas oil) was only 19.3 wt.%. The non-gas product formed a hard wax which could flow only at about 80°C. At 460°C, the major product was a soft gel at room temperature. A fluid liquid product could only be obtained at 470°C. The product yields in Table 3 follow a certain pattern, i.e., as the temperature increased, yields of gaseous product, naphtha and THFI increased at the expense of residue yield. The gas oil yield increased with temperature up to 470°C, then started to decline. At 500°C, gas and THFI yields increased sharply due, in part, to overcracking of naphtha. The "loss" in Table 3 refers to the unrecovered low boiling point compounds, e.g., C₅ and C₆. Thus, the naphtha yield in Table 3 could be higher than indicated. The THFI are essentially coke produced at high temperature. Coke formation and accumulation on the reactor wall may hamper heat transfer and cause operating problems in a plant.

The composition of gaseous product (Figure 1) indicates that: 1- n-alkanes predominated with over 85 wt.% C₁ to n-C₄ at high temperatures (480-500°C). Among the n-alkanes, C₁ and C₂ increased at the expense of C₄ at 450-470°C while C₃ remained relatively constant throughout the temperature range; 2- olefin and hydrogen yields decreased with increased temperature. This could be visualized as more and more olefins were recombined to form larger molecules or be saturated by hydrogen at high temperature and pressure in a closed reactor; 3- very little branched hydrocarbons, e.g., iso-butane and iso-butylene, were found as shown also in Table 3. This is a typical example of thermal cracking of waxy paraffin reported in the early literature (17).

The composition of C₄-C₁₀ in naphtha (Figure 2) shows a gradual decrease in normal saturates (a predominant component) with increased temperature. This was balanced out by the increases in both branched and cyclic saturates giving a relatively constant level of total saturates. With increasing reaction temperature, normal 1-olefins (classified as α-olefins) decreased from 27.0 to 3.3 wt.% while monoaromatics increased from 1.1 to 25 wt.% at 450°C and 500°C, respectively. The combined branched olefins (could also be α-olefins) and normal internal olefins (n-olefins with double bond not at the terminal position), and cyclic olefins showed a small increase followed by a slight decline as temperature increased. These gave an overall decrease in olefins with increased temperature. Alkadienes were detected at 450 and 460°C but not at higher temperature except in the gas oil fraction. It should be noted that GC-MS analysis cannot differentiate branched olefins from normal internal olefins. In order to determine the amount of branched olefins, naphtha at 480°C was hydrogenated over a Pt/Al₂O₃ catalyst to form normal and branched alkanes and cyclic compounds including aromatics. By comparing the GC analyses of the feed and its hydrogenated product, the content of branched olefins in the C₄-C₁₀ liquid product at 480°C was estimated at 4-5 wt.% (out of 11 wt.%).

Assuming that C₄-C₁₀ hydrocarbons constitute 100 wt.% of naphtha (220°C-), a further breakdown into its structural yields can be obtained as shown in Table 3. It can be seen that following the increase in temperature, the saturates (normal, branched and cyclic alkanes) and

monoaromatics increased steadily except at 500°C where overcracking of the saturates might occur. The overall olefin yield also increased but reached a maximum at 490°C after which it began to decline. The ratio of normal 1-olefins to normal alkanes dropped from 0.31 at 470°C to 0.10 at 500°C. This suggests that in closed system secondary reactions such as isomerization, cyclization, aromatization and hydrogenation of olefins prevailed at high temperature, in addition to the primary cracking of long chain compounds. This resulted in a decrease in olefins (especially normal 1-olefins), the disappearance of alkadienes and an increase in monoaromatics.

It seems that optimum product yields were obtained between 470 and 490°C with higher distillate yield and lower coke yield. At 500°C, gas (especially low value methane and ethane) and coke yields increased sharply at the expense of distillate yield. Below 470°C, the residue content was too high after 10 min reaction. Separate tests indicated that an increase in reaction time had a significant effect on distillate yield at lower temperature. For example, by increasing reaction time from 10 to 30 min, the hard wax produced at 450°C became a viscous liquid whereas the soft gel formed at 460°C turned into a fluid liquid. Gas (mostly methane, ethane and propane) yield increased and suspension of coke particles was observed.

Although pyrolysis of HDPE at 470-490°C in a closed system can produce a high yield of distillates, it is expected that they are poor in quality and further treatment is necessary to make them acceptable as transportation fuels. The normal alkanes in naphtha have low octane numbers (18). The gum-forming alkadienes in gas oil make it unstable with less value although light gas oil may have a high cetane number due to its low aromatics content. Despite these drawbacks, the pyrolytic distillates may be useful in other applications such as producing long chain α -olefins which are important feedstocks to fabricate comonomers, detergents, plasticizers, synthetic lubricants and other fine chemicals.

Thermal cracking of HDPE in an open system

Since nitrogen was used as a carrier gas in the open system, products from primary cracking below the desired temperature could be purged out of the reactor thus reducing secondary reactions.

Consequently, the predominant product was gas oil which was prevented from further cracking in the reactor. This was accompanied by reduced formation of gas, naphtha and residue compared with those from the closed system. Figure 3 shows a comparison of product distribution of thermal cracking of HDPE in two different systems at 480°C which was actually the final reaction temperature. As can be seen, gas oil was the major product in the open system which apparently had higher material loss possibly because of high flow of carrier gas.

Distillates from the two systems at 480°C were further characterized by HPLC. The results in Figure 4 indicate that: (1) the open system produced very little aromatics, less saturates but more olefins in both naphtha and gas oil fractions compared with the corresponding distillates from the closed system. This again resulted from the reduction of secondary reactions in the open system; (2) for the same reaction system (open or closed), the composition of naphtha was similar to that of the gas oil fraction except naphtha from the closed system contained slightly less aromatics but slightly more olefins whereas naphtha from the open system contained slightly less olefins, compared with their corresponding gas oil fraction.

The naphtha fractions separated by HPLC were further characterized by GC-MS for structural analysis. The results are illustrated in Figure 5 which shows that in the open system normal 1-olefins were the most predominant product (40 vs 8.7 wt.% from the closed system), followed by n-saturates (27 vs 42 wt.%), cyclic- + di-olefins (15 vs 7.8 wt.%), cyclic saturates (10 vs 16 wt.%), branched + normal internal olefins (6 vs 11 wt.%), monoaromatics (1 vs 10 wt.%) and branched saturates (0.9 vs 4.3 wt.%). Again, this confirms the diminishing secondary reactions in the open system. From these analyses, one may also conclude that the distillates from the open system can hardly meet the specifications of transportation fuels.

Catalytic cracking of waxy pyrolytic products from tubing bomb reactor

Catalytic cracking is a possible route to upgrade the heavy pyrolytic product from PE into transportation fuels. Three waxes were chosen as shown in Table 1. The fractions in boiling range of naphtha (IBP-216°C), LCO (216-343°C) and HCO (343°C+) are: 18.0, 25 and 57 wt.% for wax A, 20.2, 29.3 and 50.5 wt.% for B, and 28.2, 37.8 and 34 wt % for C, respectively. Due to small volumes of waxy products available from the tubing bomb tests, the naphtha fractions were not removed prior to MAT evaluation. Wax A was mostly catalytically cracked at 510°C and B and C at 470°C with WHSV at 20 h⁻¹. Three tests were particularly performed at low severity (470°C, about 300 h⁻¹ WHSV and 0.5 cat/oil ratio) to increase the middle distillate production. Cracking results along with PIONA and octane analyses of gasolines produced are shown in Tables 4 and 5. Key observations are:

- The three waxes are highly crackable with over 80+ wt.% conversion at medium severity. The products are characteristic of low yields of dry gas, HCO and coke but high yields of LPG (B and C produced less LPG) and gasoline. LCO could be increased at low severity still with reasonable gasoline production.
- Contrary to the pyrolysis, catalytic cracking of PE-derived waxes produced significant amounts of isobutane, isobutylene, branched paraffins and olefins in the gasoline range. This is attributable to: (1) rapid skeletal isomerization of primary and secondary carbenium ions to the most stable tertiary type prior to β -scission (19); (2) the much faster hydrogen transfer to tertiary olefins than to n-olefins (20). These iso-type hydrocarbons are either high octane gasoline components or important feedstocks to produce alkylates and octane boosters, e.g., MTBE, ETBE and TAME. Except those runs with very high conversion, the aromatics contents in gasolines are below the phase II limit (25 vol.%, to be in effect in 1996) high octane gasoline components or important feedstocks to produce alkylates and octane boosters, e.g., MTBE, ETBE and TAME. Except those runs with very high conversion, the aromatics contents in gasolines are below the phase II limit (25 vol.%, to be in effect in 1996) in California's Reformulated Gasoline Program (21).

- PIONA analyses of gasolines show a general trend that for the same feedstock iso-paraffins and monoaromatics increased at the expense of olefins as conversion increased. This is consistent with the observations reported previously (22 and 23). Generally, such a change in PIONA distribution resulted in higher octane numbers at increased conversion (22). Note that olefins are the most reactive components in gasoline, they can undergo several hydrogen transfer reactions effecting a decrease in olefins and an increase in paraffins, aromatics and naphthenes (24):

Olefins + Naphthenes —————→ Paraffins + Aromatics

Olefins —————→ Paraffins + Aromatics

Cyclo-olefins —————→ Naphthenes + Aromatics

- Tables 4 and 5 indicate that among the three MAT feeds, wax A was the most reactive as reflected by the highest conversion of 59.9 wt.% in the low severity runs. This was followed by B and C with conversions of 47.7 and 45.1 wt.%, respectively, at the same conditions. The reactivities of these feeds were in the reverse order of their lightness in terms of boiling point. This is explained by the fact that the three waxes derived from the same source (PE) are mostly composed of straight chain hydrocarbons containing no poisons, e.g., nitrogen and coke precursor, to the catalyst. Thus, the reaction rate depends on the chain length (or carbon number) of the molecules. According to Voge (25), for the same hydrocarbon type, the higher the carbon number the more reactive the molecules. This explains why wax A is more reactive than the other two. Also, data for the three low severity runs (Tables 4 and 5) indicate that a great portion of the original naphtha in the feed was not cracked to smaller molecules as dry gas and LPG.

- Compared with naphthas obtained from pyrolyses of PE, catalytically cracked gasolines definitely had improvements in octane rating. However, GC octanes of gasolines from the three low severity runs were still less than satisfactory, especially the GC RONs. The road octane numbers (average of RON and MON) of gasolines from waxes A, B and C were 78.4, 76.5 and 73.0, respectively. These values were lower than the required number of 87 for regular grade gasoline sold in service stations. This was attributable to the large fractions of straight chain compounds and relatively small fractions of aromatics in the gasolines (gasolines from A, B and C contained 17.2, 20.3 and 21.7 wt.% n-paraffins, 6.9, 19.7 and 24.1 wt.% n-olefins, and 17.3, 11.3 and 8.6 wt.% aromatics, respectively). A MAT run on wax A at higher severity (510°C, 3.99 cat/oil and 20.0 h⁻¹, Table 4) gave 10.6, 4.8 and 24.5 wt.% n-paraffins, n-olefins and aromatics, respectively, leading to a road octane number of 81.5 which is closer to the desired value. With some sacrifice of gasoline yield, octane numbers can be improved considerably by adding a small amount of shape-selective zeolite ZSM-5 (0.5-2 wt.%) to the cracking catalyst to crack and isomerize C₇-C₁₃ normal compounds to branched C₃-C₅ olefins (26).
- Some overcracking of wax A seemed to occur at high severity as reflected by the lower gasoline yield but higher yields of dry gas, LPG and coke as the conversion exceeded 90 wt.% (Table 4). It was felt that a better product distribution would have been obtained if wax A were cracked at a lower temperature such as 490 or 470°C. Nevertheless, all three feeds could produce very high gasoline yields with small amounts of low value products (especially HCO). The product slates are, in general, better than those from the conventional light crude vacuum gas oils such as BC Light (from British Columbia, Canada) under equivalent conversion (27). The reason is that the waxes are essentially free of problematic species and low in aromatics of which the benzene rings are not crackable at FCC conditions. The quality of LCO was not yet determined. Its aromatics content was higher than that of the gasoline but no di-olefins were detected. Usually, the quality of LCO can be improved at a lower conversion (28).

It is thus concluded that low grade pyrolytic waxy products can be catalytically cracked to high yields of gasoline of improved octane rating. However, the viability of the plastic waste conversion technology through this route depends on many factors such as technical improvement, pretreatment of the plastic wastes including sorting, cleaning and shredding of polyethylene products, profitability of the two-step conversion process and practicality of pyrolyzing only the "clean" plastics containing no harmful ingredients or contaminants, etc. Our in-house studies indicate that polypropylene and polystyrene can be treated in a similar manner and the same objective can be achieved. This will widen the scope of application of this technology.

CONCLUSIONS

PE could be thermally decomposed at and above 450°C. Higher temperature produced more distillates but gas and coke yields also increased. In a closed reaction system, overcracking of naphtha was observed at 500°C. Optimum temperature for distillate production was found at 470-490°C. Compared with the closed system at the same temperature, the open system produced less naphtha and more gas oil. With respect to hydrocarbon type, the open system produced more olefins (even diolefins), less saturates and very little aromatics. For the same reaction system, both naphtha and gas oil fractions had similar compound types. While pyrolysis of PE produced low grade transportation fuels which required further upgrading, catalytic cracking of the pyrolytic waxy product produced high yields of gasoline of better quality and LPG with little dry gas, coke and heavy cycle oil. The viability of this two stage conversion technique depends on process economics and future regulatory considerations.

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Nomenclature and definition

PIONA = Paraffins, isoparaffins, olefins, naphthenes and aromatics

WHSV = g oil injected/h x g catalyst

Conversion = 100 - (LCO + HCO)

Dry gas = H₂ + H₂S + CH₄ + C₂

LPG = C₃ + C₄

Gasoline = FCC liquid product (C₅ to 216°C)

LCO = FCC liquid product (216-343°C)

HCO = FCC liquid product (343°C+)

Coke = 1.1 x carbon content of spent catalyst

MTBE = Methyl tertiarybutyl ether

ETBE = Ethyl tertiarybutyl ether

TAME = Tertiary amyl methyl ether

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TABLE 1 - Feedstock Analysis

Feedstock	Polyethylene		Wax		
	HDPE	LDPE	XX A	B	C
Specific Gravity	0.890-0.965				
C, wt. %	85.3	84.9	85.1	85.1	85.2
H, wt. %	13.9	13.9	13.8	14.0	13.9
Total N, wt. %	-	0.03	-	-	-
Total S, wt. %	-	0.04	-	-	-
Boiling Range by GCD, °C					
IBP			71	71	39
10			172	168	133
20			230	214	190
30			281	267	228
50			373	344	297
70			461	413	355
90			549	495	417
FBP			627	598	519
GC Analysis, wt. %					
n-Paraffins			76.8	38.6	36.2
α -Olefins			18.1	34.5	42.8
Others *			5.1	26.9	21.0

* Branched and cyclic paraffins, branched, normal internal and cyclic olefins, alkadienes and aromatics.

TABLE 2 - Analysis of Equilibrium Cracking Catalyst

Catalyst	KOB-627
Type	USY
BET Surface Area, m ² /g	195
Zeolite Surface Area, m ² /g	135
Relative Zeolite Content, wt. %	19.9
Matrix Pore Volume, mL/g	0.28
Matrix Av. Pore Diameter, Å	176
V, wppm	300
Ni, wppm	150
Al ₂ O ₃ , wt. %	30.1
Unit Cell Dimension, Å	24.25

TABLE 3- Thermal Cracking of HDPE in Closed Tubing Bomb Reactor

Temperature, °C	450	460	470	480	490	500
Yields, wt.%						
Gas (H ₂ -C ₄)	0.8	1.7	4.5	7.7	13.5	23.0
Naphtha	5.4	9.5	37.4	44.7	52.1	44.3
Gas Oil	13.9	21.2	39.6	30.1	23.8	12.1
Residue	79.4	66.1	16.8	11.3	4.2	8.6
THFI	0.0	0.0	0.0	0.1	1.0	2.8
Loss	0.5	1.5	1.7	6.1	5.4	9.2
Gas Yield, wt.%						
H ₂	0.00	0.01	0.03	0.04	0.05	0.06
C ₁	0.05	0.14	0.72	1.54	2.73	5.20
C ₂	0.11	0.28	1.29	1.98	3.79	6.37
C ₂ =	0.03	0.06	0.08	0.10	0.09	0.09
C ₃	0.22	0.49	1.34	2.52	4.59	8.03
C ₃ =	0.17	0.35	0.45	0.57	0.54	0.55
n-C ₄	0.11	0.20	0.36	0.61	1.15	1.88
i-C ₄	0.00	0.01	0.02	0.05	0.17	0.38
C ₄ =	0.11	0.17	0.22	0.31	0.40	0.45
C₄-C₁₀ Liq. Yield, wt.%						
Saturates	3.05	5.54	22.0	27.9	32.7	25.7
Normal	2.48	4.28	15.7	18.8	20.8	15.1
Branched	0.08	0.14	1.08	1.92	3.07	3.50
Cyclic	0.49	1.12	5.19	7.24	8.75	7.09
Olefins	2.30	3.71	12.8	12.3	18.2	7.55
Normal, 1-	1.46	2.00	4.86	3.89	9.79	1.46
Branched + Nor.I.*	0.36	0.70	4.86	4.92	5.21	3.83

Table 3 (cont'd)

Temperature, °C	450	460	470	480	490	500
Monoaromatics	0.06	0.25	2.62	4.47	8.34	11.1

* Normal Internal

TABLE 4 - Catalytic Cracking of Wax A from Pyrolysis of LDPE in Closed System

Temperature, °C	470	510	510	510
Cat/Oil, wt./wt.	0.43	2.52	3.99	6.10
WHSV, h ⁻¹	333	19.8	20.0	19.69
Yields, wt. %				
Dry Gas	1.22	1.83	1.81	2.20
LPG	10.61	17.76	22.39	25.72
C ₃	0.59	1.33	1.44	1.72
C ₃ =	2.84	4.40	6.57	7.56
n-C ₄	0.53	1.14	1.19	1.35
i-C ₄	2.13	6.69	5.77	7.43
C ₄ =	4.52	4.20	7.43	7.67
Gasoline	45.9	63.2	63.0	59.6
LCO	22.8	14.0	8.8	7.8
HCO	17.3	1.9	1.3	1.2
Coke	1.8	1.3	2.4	3.0
Conversion, wt. %	59.9	80.1	89.9	91.0
Composition of C ₄ -C ₁₁ in Gasoline, wt. %				
P (n-Paraffins)	17.2		10.6	
I (i-Paraffins)	12.6		31.2	
O (Olefins)	38.5		18.2	
N (Naphthenes)	14.4		15.6	
A (Aromatics)	17.3		24.5	
GC RON	80.1		85.0	
GC MON	76.6		77.9	

TABLE 5 - Catalytic Cracking of Waxes B and C from Pyrolysis of HDPE in Open System

Feed	Wax B			Wax C				
Temperature, °C	470	470	470	470	470	470	470	470
Cat/Oil, wt./wt.	0.47	2.68	4.15	0.48	2.95	3.02	3.70	4.20
WHSV, h ⁻¹	308	18.6	19.3	298	18.1	19.2	19.8	19.0
Yields, wt.%								
Dry Gas	0.62	0.64	0.95	0.18	0.27	0.30	0.58	0.59
LPG	6.31	10.8	17.4	3.46	6.49	6.74	10.6	14.6
C ₃	0.29	0.54	0.65	0.11	0.24	0.28	0.49	0.57
C ₃ =	1.81	2.45	4.84	0.95	1.57	1.58	2.38	4.34
n-C ₄	0.22	0.49	0.71	0.14	0.28	0.32	0.47	0.54
i-C ₄	1.37	4.50	5.87	0.78	2.36	2.57	4.37	4.44
C ₄ =	2.62	2.86	5.33	1.47	2.14	1.98	2.87	4.73
Gasoline	39.2	60.4	67.7	40.9	60.5	61.2	62.5	64.0
LCO	27.3	21.5	10.7	33.0	26.0	25.6	21.1	10.8
HCO	25.1	4.4	1.3	21.9	5.5	4.6	3.2	6.9
Coke	1.4	2.2	1.9	0.5	1.2	1.5	2.1	3.2
Conversion, wt.%	47.7	74.1	88.0	45.1	68.5	69.7	75.8	82.4
Composition of C ₄ -C ₁₁ in Gasoline, wt.%								
P (n-Paraffins)	20.3	14.4	14.9	21.7	16.4	15.8	13.9	17.3
I (i-Paraffins)	12.2	45.1	47.7	10.2	39.2	39.3	45.8	46.1
O (Olefins)	43.4	16.4	15.4	45.2	21.1	21.7	16.6	13.4
N (Naphthenes)	12.8	12.1	11.3	14.3	13.6	13.2	11.7	12.0
A (Aromatics)	11.3	12.0	10.6	8.6	9.7	10.0	12.0	11.2
GC RON	74.8			70.7				
GC MON	78.2			75.2				

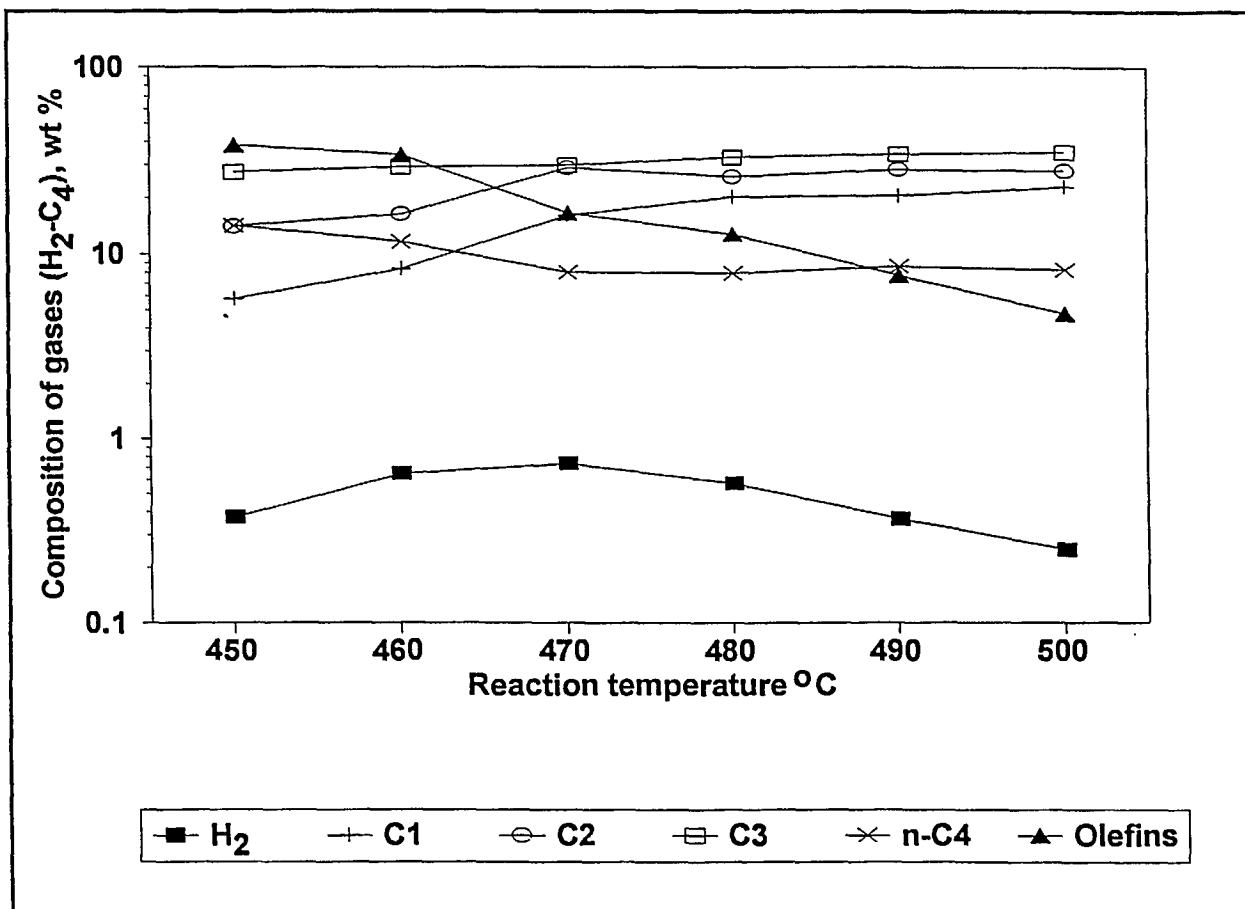


Figure 1 - Effect of reaction temperature on composition of gaseous product from pyrolysis of HDPE in closed tubing bomb reactor.

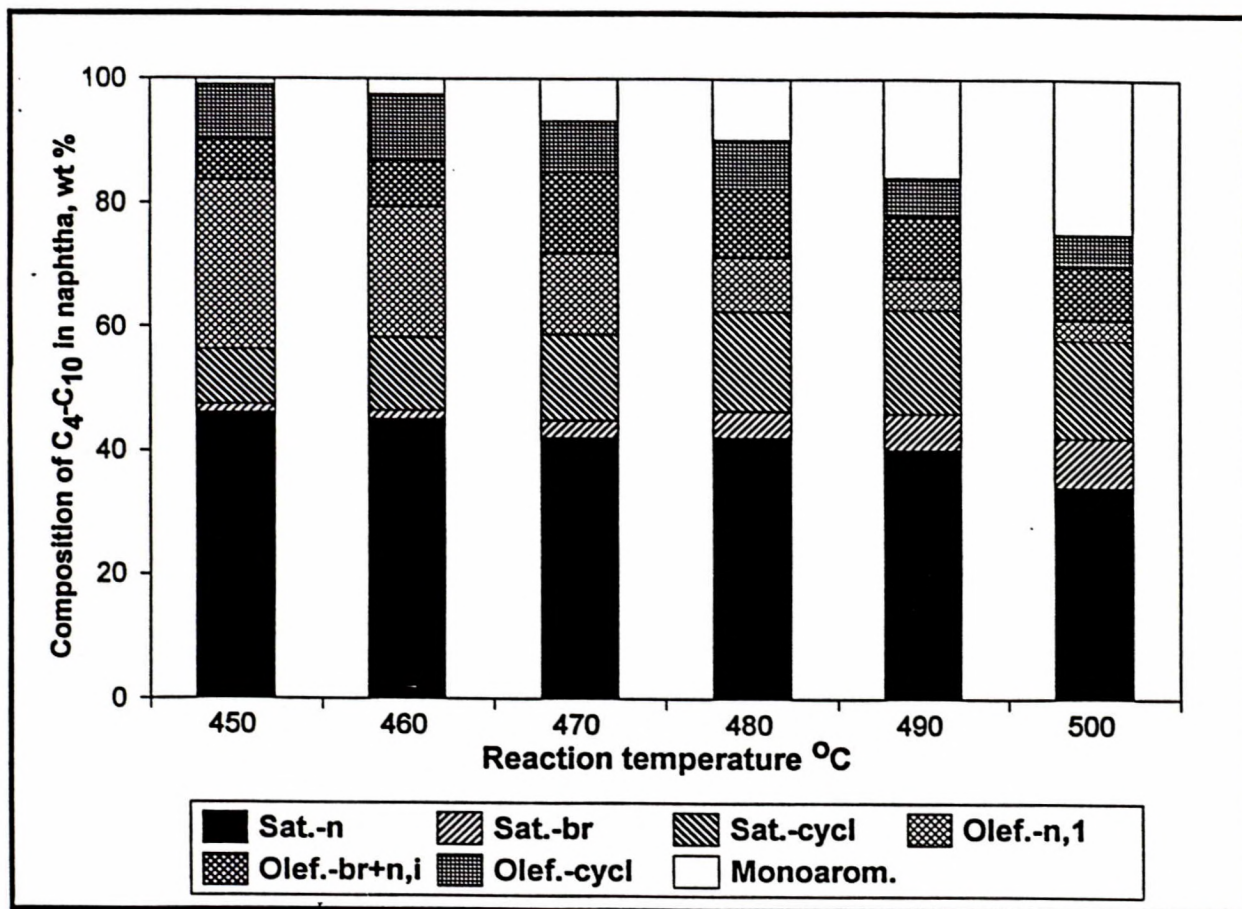


Figure 2 - Effect of reaction temperature on composition of C₄-C₁₀ in naphtha from pyrolysis of HDPE in closed tubing bomb reactor.

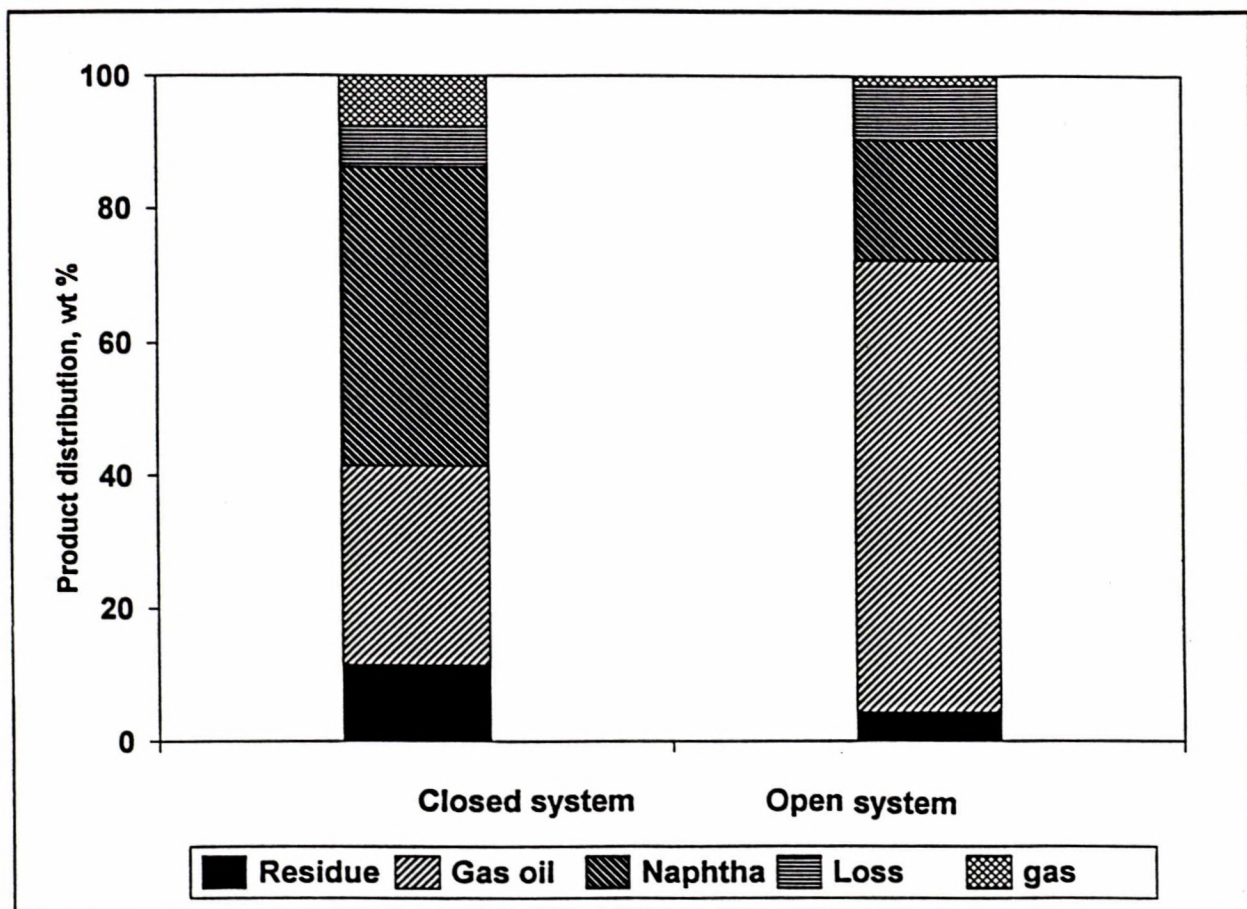


Figure 3 - Comparison of product distribution between closed and open reaction systems at 480°C.

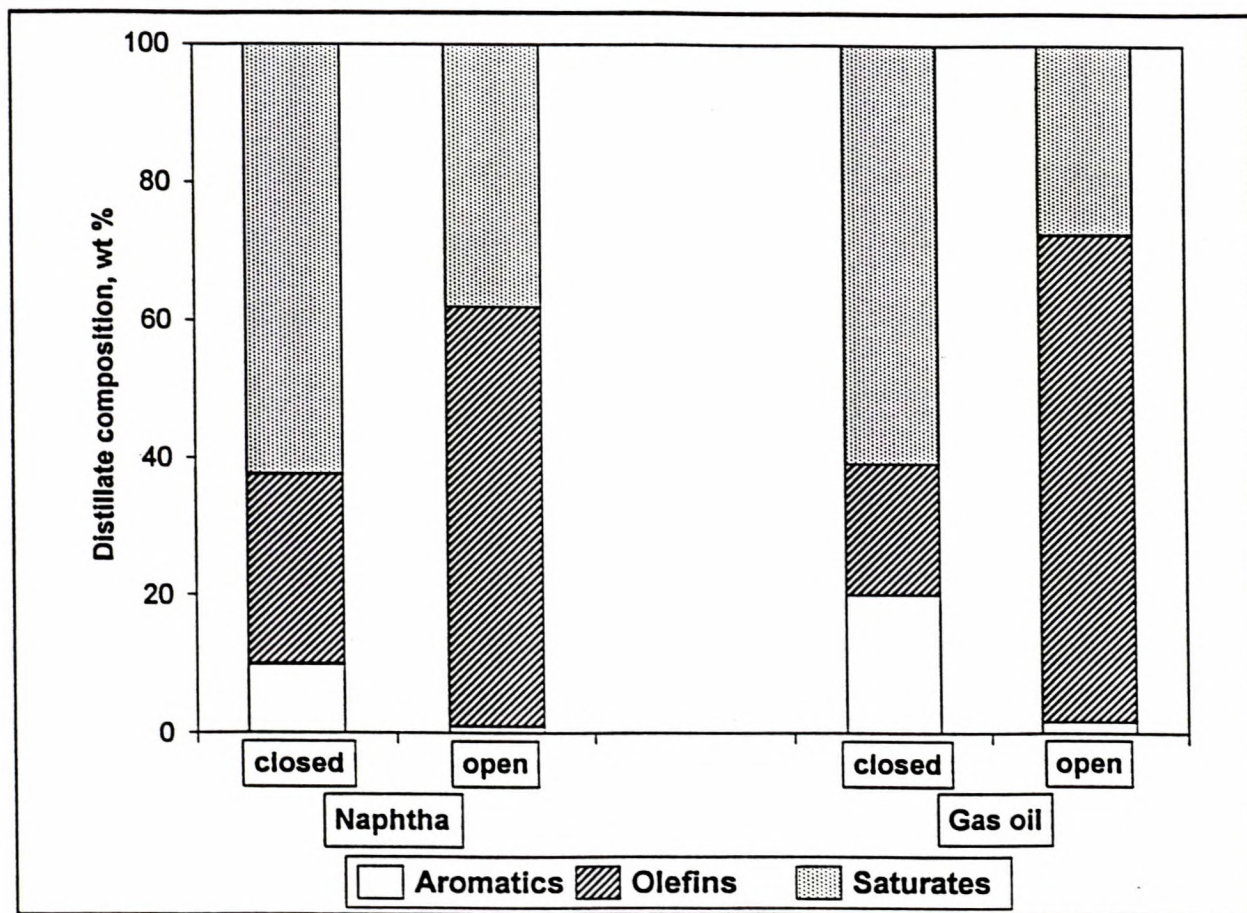


Figure 4 - Comparison of distillate composition between closed and open reaction systems at 480°C.

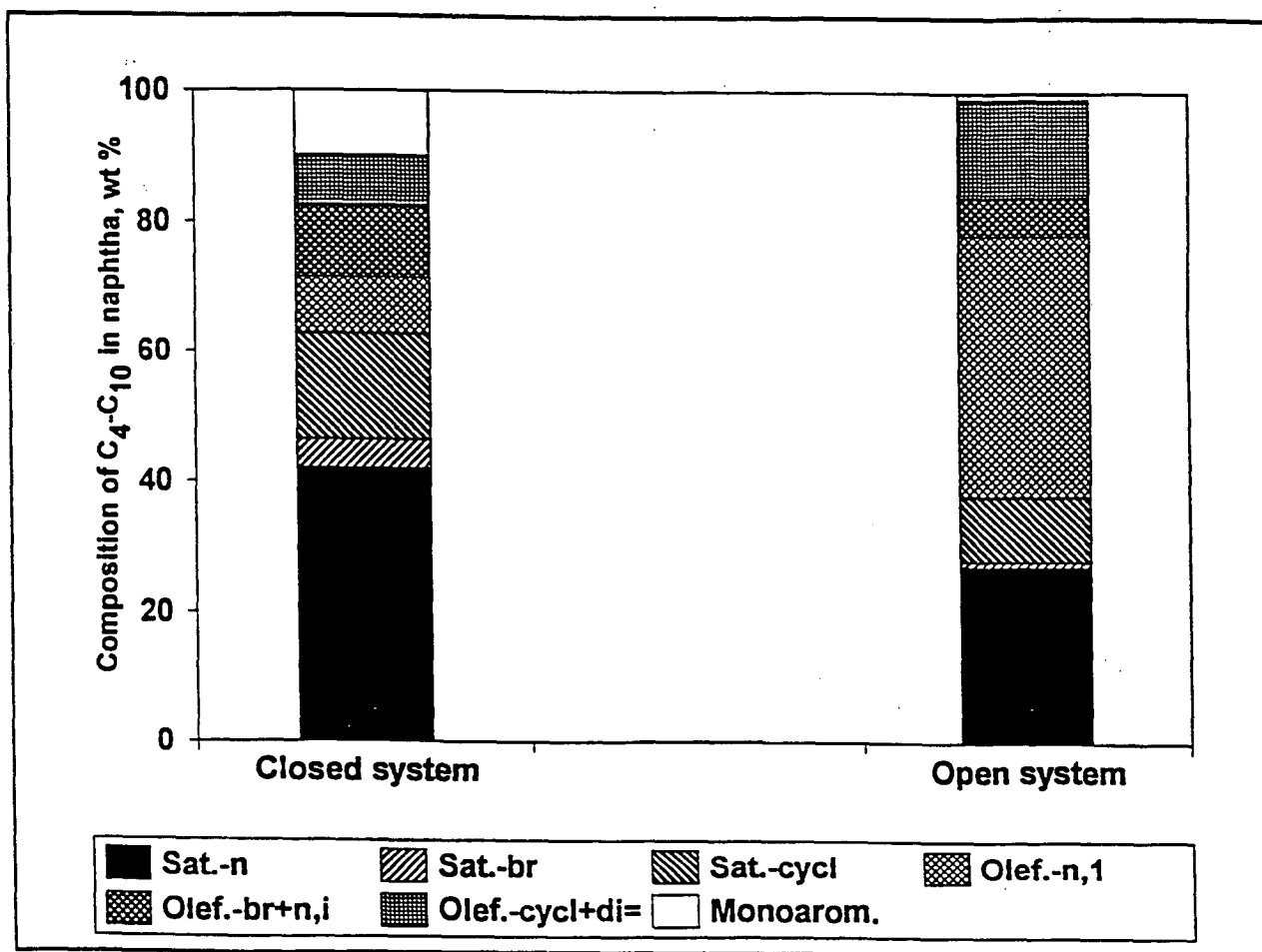


Figure 5 - Comparison of composition of C₄-C₁₀ in naphtha between closed and open reaction systems at 480°C.