Heavy Oil/Plastic Co-Processing - Subtask 4.1

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ABSTRACT

Western Research Institute (WRI) is developing a low-temperature thermal decomposition process to alleviate the problems associated with disposal of waste plastics and at the same time generate a product stream in the gasoline boiling range for use in the refining and petrochemical industries. The technology being developed by WRI is significantly different from conventional thermal decomposition processes used to recover distillates from waste plastics. The key to this difference is the application of a decomposition initiator concept that allows operation of the process at temperatures below those used in other thermal decomposition processes. The WRI technology utilizes the decomposition initiator to enhance thermal decomposition of waste plastics in the presence of a low-value heavy oil at temperatures below those normally used for thermal decomposition. Operation of the process at lower temperatures produces higher yields of distillate product and lower yields of gaseous and char products than conventional processes.

The activity of the initiator was identified in earlier research studying the thermal decomposition of polymers. This activity was observed to result in a decrease in the temperature required to thermally decompose plastics in the presence of a heavy oil. These early experiments indicated that the initiator was native to the plastics matrix, but the identity and possible mode of action were not determined. This study was undertaken to identify the active initiator in the plastics matrix and define its activity. The experiments performed in this study were conducted in a batch-type reactor. The particular elements of the activity that were addressed included: (1) the kinetics of the reaction, (2) the effects of diluting the plastics with the heavy oil, and (3) the effects of using different types of heavy oil.

The investigation identified polyvinyl chloride as the active component in the reaction matrix responsible for the observed reduction in the thermal decomposition temperature. In addition, higher plastics conversions were obtained with more dilute solutions of plastics in the heavy oil, and heavy oils such as fluidized-bed catalytic cracker heavy recycle oil promote plastics conversion to a greater extent than more aliphatic oils such as SAE 50 weight motor oil.

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EXECUTIVE SUMMARY

The United States generates in excess of 160 million tons of municipal solid waste or garbage each year. Of this mass, plastics represent about 7% or 11 million tons. Disposal of these wastes is becoming a serious problem because landfill site capacity is decreasing. In the last ten years, the number of landfill sites has dropped from 18,500 to 6,000. This decrease has placed an additional burden on municipalities the disposal of solid wastes. The problem will become more serious in the future as states begin to pass more stringent legislation regulating landfill disposal. The only practical solution to this problem is to decrease the volume of material being disposed of in landfill sites through rigorous conservation and recycling efforts.

Plastics represent one segment of solid wastes that can be recycled to decrease the mass of solids and yield value-added products. Conventional approaches to address recycling of municipal waste plastics rely on secondary or tertiary recycling processes (Ehrig 1992). Secondary recycling processes recycle the bulk plastics back to the plastics industry for the manufacture of new products. Tertiary recycling processes utilize plastic wastes as a carbon-containing resource and thermally process the plastics to produce a low-molecular-weight distillate.

Secondary recycling of waste plastic involves collection, sorting, reclamation, and reuse of the plastic material. There are several problems associated with large-scale secondary recycling anticipated in the future. The first problem is the separation of bulk waste plastic into individual polymer types for recycling, which is normally done manually, and is costly. The second problem is critical to the health and safety of our society. This is the possible contamination of the plastic with organic material associated with the plastic. This is particularly true for plastic wastes from the food service industry, chemical laboratories, and hospitals where, in some cases, the contaminants associated with the plastic may be classed as hazardous wastes.

A third problem is developing markets for recycled plastics. Current efforts have been directed at replacing virgin plastics with recycled plastics in the manufacture of more durable goods, such as park benches, curb stops, and building materials. For this reason, the market for recycled plastics may be limited and easily saturated if large scale recycling becomes a reality. This will decrease the economic benefit of recycling and discourage this conservation effort.

An alternative philosophy is to convert the polymeric structure to smaller chemical molecules such as the monomeric units and related chemical structures (tertiary recycling). This improves the market for the products because the market is not a "to-be-developed" manufacturing process, but existing plants in the refining and petrochemical industries.

WRI is developing a low-temperature thermal decomposition process to alleviate the problems associated with disposal of waste plastics and at the same time generate a product stream in the gasoline boiling range for use in the refining and petrochemical industries. The technology is significantly different from conventional thermal decomposition processes used to recover distillates from waste plastics. The key to this difference is the application of a decomposition initiator concept that allows operation of the process at temperatures below those used in other thermal decomposition processes. The WRI technology utilizes the decomposition initiator to enhance thermal decomposition of waste plastics in the presence of a low-value heavy oil at temperatures below those normally used for thermal decomposition. Operation of the process at lower temperatures produces higher yields of distillate product and lower yields of gaseous and char products than conventional processes.

The activity of the initiator was identified in earlier research studying the thermal decomposition of polymers. The activity was first observed as a decrease in the temperature required to thermally decompose plastics in the presence of a heavy oil. These early experiments indicated that the initiator was native to the plastics matrix, but the identity and possible mode of action were not determined.

This study was undertaken to identify the active initiator in the plastics matrix and define its activity. The experiments performed in this study were conducted in a batch-type reactor. The particular elements of the activity that were addressed included: (1) the kinetics of the reaction, (2) the effects of diluting the plastics with the heavy oil, and (3) the effects of using different types of heavy oil.

The results identified from this investigation can be summarized as follows:

1. The component in the reaction matrix responsible for the observed reduction in the thermal decomposition temperature is polyvinyl chloride.

2. Higher plastics conversions are obtained with more dilute solutions of the plastic in the heavy oil.
3. Heavy oils such as fluidized-bed catalytic cracker heavy recycle oil promote plastics conversion to a greater extent than do more aliphatic oils such as SAE 50 weight motor oil.
4. The mode of action of polyvinyl chloride in reducing the reaction temperature for thermal decomposition of waste plastics appears to be that of a free radical initiator.

INTRODUCTION

Western Research Institute is developing a low-temperature thermal decomposition process to alleviate the problems associated with disposal of waste plastics and at the same time generate a product stream in the gasoline boiling range for use in the refining and petrochemical industries. This process is an economical alternative to landfill disposal and provides the opportunity for a profitable business venture.

The United States generates in excess of 160 million tons of municipal solid waste or garbage each year. Of this mass, plastics represent about 7% or 11 million tons. Disposal of these wastes is becoming a serious problem because landfill site capacity is decreasing. In the last ten years, the number of landfill sites has dropped from 18,500 to 6,000. This decrease has placed an additional burden on municipalities for the disposal of solid wastes. The problem will become more serious in the future as states begin to pass more stringent legislation regulating landfill disposal. The only practical solution to this problem is to decrease the volume of material being disposed of in landfill sites through rigorous conservation and recycling efforts.

Plastics represent one segment of solid wastes that can be recycled to decrease the mass of solids and yield value-added products. Conventional approaches to the recycling of municipal waste plastics rely on secondary or tertiary recycling processes (Ehrig 1992). Secondary recycling processes recycle the bulk plastics back to the plastics industry for the manufacture of new products. Tertiary recycling processes utilize plastic wastes as a carbon-containing resource and thermally process the plastics to produce a low-molecular-weight distillate.

Secondary recycling of waste plastic involves collection, sorting, reclamation, and reuse of the plastic material. Several recycling efforts have been instituted across the country and are receiving a great deal of community support. However, there are several problems associated with large-scale, secondary recycling anticipated in the future. The first problem is the separation of bulk waste plastic into individual polymer types, which is necessary to ensure the quality of the products manufactured from the recycled plastic. This separation is normally done manually and is costly. This will affect the price of products manufactured from recycled plastic and decrease the economic advantage of using recycled plastic.

The second problem is critical to the health and safety of our society. This is the possible contamination of the plastic with organic material associated with the plastic. Waste plastic has material associated with it that is difficult and costly to remove in the reclamation step of secondary recycling processes. This is particularly true for plastic wastes from the food service industry, chemical laboratories, and hospitals where, in some cases, the contaminants associated with the plastic may be classed as hazardous wastes. This hazardous waste can be introduced into society through products made from recycled plastic.

A third problem is developing markets for recycled plastics. Current efforts have been directed toward replacing virgin plastics with recycled plastics in the manufacture of more durable goods, such as park benches, curb stops, and building materials. As yet, recycled plastics have not been widely introduced into the consumer packaging industry. Currently, there are no restrictions on the use of recycled plastics for use in packaging food-related items, but its acceptance by consumers is questionable. For these reasons, the market for recycled plastics may be limited and easily saturated if large-scale recycling becomes a reality. This will decrease the economic benefit of recycling and discourage this conservation effort.

An alternative philosophy that we have chosen for the recycling of waste plastics is to convert the polymeric structure to smaller chemical molecules such as the monomeric units and related chemical structures (tertiary recycling). This improves the market for the products because the market is not a "to-be-developed" manufacturing process but existing plants in the refining and petrochemical industries, which are already experiencing limited supplies of low molecular-weight, heteroatomic free feedstocks from petroleum crude oils.

The low-molecular weight distillate from plastics has potential as a gasoline blending stock for the production of unleaded gasoline. Low-temperature thermal decomposition of the 11 million tons of waste plastic discarded each year would produce 56 million barrels of gasoline blending stock, or 153 thousand barrels per day. Considering this contribution in light of our energy pool and average gasoline imports provides a realistic perspective of the economic importance of this product. Using data provided by the U.S. Department of Energy (1990), the average volume of gasoline imported over seven years (through 1990) is 356 thousand barrels per day. The distillate product from low-temperature thermal decomposition of waste plastics

represents 43 percent of our average gasoline imports. This is a substantial percentage of our gasoline imports and will have significant impact on our foreign import of gasoline.

BACKGROUND

Waste plastics present a potentially serious problem because of the need for disposal or reuse of this waste. To address this end, WRI has been evaluating recycling options to recover marketable products from the waste plastic stream (Guffey et al. 1991). Conventional recycling approaches are limited by the need to separate the waste into individual plastic types or to develop a market for the products manufactured from recycled plastics (Ehrig 1992). Western Research Institute initiated development of its own process to avoid these limitations. Currently, WRI holds a patent position for a low-temperature, thermal decomposition process for recycling waste plastics, and more filings are planned. The developmental efforts are addressing the processing of municipal waste plastics to produce a hydrocarbon stream in the gasoline and diesel fuel boiling ranges for use in the refining and petrochemical industries.

The technology being developed by WRI is significantly different from conventional thermal decomposition processes used to recover distillates from waste plastics. The key to this difference is the application of a decomposition initiator that allows operation of the process at temperatures below those used in other thermal decomposition processes. The WRI technology utilizes the decomposition initiator to enhance thermal decomposition of waste plastics in the presence of a low-value heavy oil at temperatures below those normally used for thermal decomposition. Operation of the process at lower temperatures produces higher yields of distillate product and lower yields of gaseous and char products than conventional processes.

The activity of the initiator was identified in earlier research studying the thermal decomposition of polymers. The activity of the initiator was first observed as a decrease in the temperature required to thermally decompose plastics in the presence of a heavy oil. These early experiments indicated that the initiator was native to the plastics matrix, but the identity and possible mode of action were not determined. This study was undertaken to identify the component in the plastic mixture responsible for the observed activity and to define this activity.

PURPOSE

The research discussed in this report was undertaken to establish the characteristics of the initiator responsible for the reduction in the thermal decomposition temperature observed during thermal coprocessing of waste plastics and a heavy oil.

METHODOLOGY

The objective of this work was to investigate the reduction in temperature observed when waste plastics are coprocessed with heavy oils. This section discusses the design and operation of the reactor systems used for this study.

Batch Reactor

The design of the batch reactor is provided in Figure 1. The reactor was constructed from a 24.1-cm (9.5-in) length of 10.2-cm (4-in) diameter schedule 40 pipe. The bottom of the reactor was sealed with a 0.6-cm (0.25-in) thick steel plate that fit inside the pipe and was welded in place to make a seal. The top of the reactor was threaded to receive a mating pipe cap. The cap was fitted with four ports to receive a thermocouple, the catalyst feed hopper, the vapor recovery line, and a line to admit nitrogen gas into the reactor. In addition, a packing gland was located in the center of the cap to accommodate the stirring shaft.

The reactor was heated with two Chromalox type HBT heaters rated at 650 J/sec (watts) each. The heaters were wired in series and controlled by Orion model E5CSX temperature controllers. Two controllers were employed in series to control the heaters. One controller was used to control the temperature of the heaters and was set to control at 468°C (875°F) because the heaters were not rated for exposure to temperatures above 482°C (900°F). The second controlled the temperature of the reaction media, and was set at the temperature designated for that experiment. Using the controllers in series protected the heaters from exposure to excessive temperatures and still controlled the temperature of the reaction media. The reactor was insulated to reduce heat losses. The temperature rise time from ambient temperature to 375°C (707°F) was 20 minutes. The temperature control at 375°C (707°F) was $\pm 3^{\circ}\text{C}$ (5°F).

Figure 1. Schematic Diagram of the Batch Reactor Used to Study the Activity of Polyvinyl Chloride

The distillate was collected as a vapor from the reactor through the vapor port in the cap of the reactor. The vapor was condensed in a water-cooled condenser and collected in a four-position cow.

The catalyst feed hopper consisted of a 1.3-cm (0.5-in) stainless steel ball valve fitted with a packing gland. The catalyst was introduced into the reactor by placing the desired mass of catalyst in a 35.6-cm x 0.6-cm (14-in x 0.25-in) stainless steel tube. The tube was inserted into the packing gland and a seal made around the tubing. The valve was opened and the tube pushed into the reactor. The catalyst was discharged from the tube with a plunger similar to a syringe. The tube was then pulled back past the valve, the valve closed, and the tube removed.

All but one of the experiments were performed in this reactor. The one experiment not conducted in this reactor utilized a smaller, all-glass reactor (Guffey et al. 1991) fitted with the same features as discussed above. The smaller reactor was used for the single experiment studying fluidized catalytic cracker heavy recycle oil. The smaller reactor was necessary because of the limited amount of this heavy oil.

Experimental Procedure

The reactor was operated by first loading it with the desired masses of waste plastic and heavy oil. The reactor was then assembled, leak checked with nitrogen gas, and insulated. The reactor was heated to the desired set point temperature (between 360 and 390°C [680 and 734°F]) and held at that temperature for the duration of the experiment. When the reactor reached the desired set point temperature, the position of the cow was changed and the catalyst added if designated for the particular experiment. Each experiment was conducted for 45 minutes, after which the cow was changed to the next position and the reactor quenched with air. For those experiments studying the kinetics of distillate production, the position of the cow was changed every 15 minutes.

The products from the experiment were collected and the mass of each measured. The residual or unreacted plastics were separated from the heavy oil by Soxhlet extraction using toluene as the solvent. The residual plastics, free from the heavy oil, were filtered to remove the excess solvent and dried in a vacuum oven at 80°C (176°F). A material balance was performed around each experiment.

Reactor Feeds

Two heavy oils were used for these experiments. The first heavy oil was SAE 50 weight oil obtained from the Amoco Oil Company. This oil was selected for the majority of the experiments performed in this study because it resembles used motor oil, and because it has been used by our laboratory to study coprocessing of plastics and tar sands. The second oil used during this study was fluidized-bed catalytic cracker heavy recycle oil (FCC). This oil was supplied by the Sinclair Refinery, Sinclair, Wyoming. It was selected because it represents a low-value refinery product, and because it is highly aromatic.

The mixture of waste plastics feed was modeled after the composition of waste plastics found in the solid municipal waste stream (Thayer 1989). The basic composition of the waste plastic mixture used for this study is listed in Table 1. The waste plastics were collected by WRI employees and manually separated by plastics type. The plastics were then reduced to 0.3-cm (0.125-in) average particle size using a laboratory blender.

Table 1. Composition of Plastics Feed Used to Model Municipal Waste Plastics

Plastic Type	Abbreviation	Weight Percentage Used
High Density Polyethylene	HDPE	34.8
Low Density Polyethylene	LDPE	36.0
Polystyrene	PS	12.4
Polypropylene	PP	11.2
Polyvinyl Chloride	PVC	5.6

RESULTS AND DISCUSSION

Material Balances

The experiments in this investigation were performed to evaluate the enhanced activity observed when waste plastics are coprocessed with a heavy oil. Since the study had this objective, studies were not performed to optimize the yield of distillate product or conversion of the waste plastic. Material balance closures were calculated for each of the experiments performed during this study. The material balance data are listed in Table 2 along with the major variables studied in each experiment. These variables include reaction temperature, presence or absence of polyvinyl chloride (PVC), the heavy oil/plastics mass ratio, and the type of heavy oil used.

The material balance closures ranged from 99.7 to 101.5%. The closures greater than 100% occurred because of the difficulty of removing toluene from the heavy oil and residual plastic. Soxhlet extraction was used to separate the heavy oil from the residual plastic. The high viscosity of the heavy oil and the solid mass of the residual plastic made solvent removal difficult and in some of the experiments trace amounts of solvent were not removed as indicated by the material balance closures greater than 100%.

Two experiments (numbers 4 and 5) were performed as duplicate experiments. The results of these experiments indicate the expected level of the experimental error. The masses of recovered distillate (49.3 and 49.5 g) are comparable. However, the masses of heavy oil (282.7 and 284.7 g) and recovered plastic (20.4 and 22.8 g) show more variation. This variation is believed to be a result of problems with the Soxhlet extraction to separate the heavy oil from the recovered plastic.

The variation in the masses of coke plus gas recovered (1.6 and 2.3 g) are due to the differences in the masses of PVC added to the reactor. The produced gas represents only a small fraction of this mass, and coke is the major product from thermal decomposition of PVC (Holman et al. 1972). Therefore, since more PVC was added to experiment 5 than to experiment 4, a higher mass of coke plus gas would be expected in experiment 5. This is the trend noted in Table 2. The results of the duplicate experiments indicate the value of the recovered distillate product is the more reliable of the values reported.

Table 2. Material Balances for the Experiments Conducted with Waste Plastics and Heavy Oil

Experiment	1	2	3	4	5	6	7	8	9	10
Temperature, °C	360	370	380	380	380	380	380	390	390	390
PVC Added	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Oil/Plastics Ratio	10:1	10:1	10:1	10:1	10:1	5:1	20:1	10:1	--	10:1
Type of Oil	SAE ^a	SAE	SAE	SAE	SAE	SAE	SAE	SAE	SAE	FCC ^b
Reactants										
Heavy Oil, g	318.8	321.8	317.4	319.9	324.2	262.6	333.3	319.6	430.1	87.5
PS, g	4.2	4.2	4.2	4.2	4.2	6.5	2.1	4.2	0.0	1.0
HDPE, g	11.8	11.8	11.8	11.8	11.8	18.2	5.8	11.8	0.0	2.7
LDPE, g	12.1	12.1	12.1	12.1	12.1	20.9	6.0	12.1	0.0	2.8
PP, g	3.8	3.8	3.8	3.8	3.8	5.8	1.9	3.8	0.0	0.9
PVC, g	2.3	2.4	0.0	2.3	4.0	2.9	1.7	2.3	1.1	0.4
Total, g	353.1	356.1	349.3	354.2	360.1	316.9	350.8	353.8	431.2	95.1
Products										
Distillate, g	19.3	27.3	35.0	49.3	49.9	43.2	42.9	95.1	49.5	5.6
Heavy Oil, g	311.2	305.1	297.3	282.7	284.7	237.1	300.0	236.1	379.5	87.2
Coke plus Gas, g	0.9	1.6	0.0	1.6	2.3	1.3	2.1	0.9	1.2	0.1
Recovered Plastic, g	25.5	24.1	17.1	20.4	22.8	39.9	11.3	22.2	0.0	2.1
Total, g	356.9	358.1	349.4	354.0	359.6	321.4	356.2	354.0	430.2	95.0
Closure, %	101.1	100.6	100.0	99.9	99.9	101.4	101.5	100.1	99.7	99.7

a SAE is SAE 50 weight motor oil

b FCC is Fluidized bed catalytic cracker heavy recycle oil

Identification of Initiator

One of the objectives of this investigation was to identify the component in the mixture of waste plastics responsible for the enhanced activity observed when waste plastics are coprocessed. A series of experiments was conducted to identify which component in the mixture was responsible for this activity. The only plastic material that enhanced the thermal decomposition activity at 380°C (716°F) was PVC.

This observation was further investigated with a series of experiments to demonstrate the effect of added PVC on distillate production, plastics conversion, and thermal decomposition temperature. One experiment was conducted at 380°C (716°F) and PVC was not added to the reaction mixture. Three experiments were conducted at 360, 370, and 380°C (680, 698, and 716°F) with the addition of 0.75 g of PVC when the reactor reached the reaction temperature. The results from these experiments are listed in Table 3, and these results include the percentage of distillate produced (based on the total charge) and the plastic conversion expressed as a weight percentage.

Table 3. Comparison of Plastics Conversion and Distillate Yields from Experiments With and Without PVC

Temperature (°C)	360	370	380	380
Initiator (PVC)	Yes	Yes	Yes	No
Plastics Conversion (%)	20.1	24.6	27.9	19.8
Total Conversion (%)	5.5	7.7	14.0	10.0

At 360°C (680°F) with the addition of PVC, distillate production and plastics conversion were 5.5% and 20.1%, respectively. The experiment conducted at 380°C (716°F) without the addition of PVC had distillate production of 10.0% and plastics conversion of 19.8%. The plastics conversion for these two experiments is comparable (approximately 20%) and shows that the 20°C (36°F) temperature increase in reaction temperature is required to accomplish the same level of plastics conversion without the addition of PVC. There is also an increase in distillate production at 380°C (716°F) without the addition of PVC as compared to 360°C (680°F) with the addition of PVC.

The addition of PVC to the reaction mixture at 380°C (716°F) increases the distillate production from 10% to 14% and increases the plastics conversion from 19.8% to 27.9%. These results demonstrate the effect noted when PVC is added to the reaction mixture of heavy oil and waste plastic. Addition of PVC promotes the thermal decomposition of waste plastics and increases the production of the distillate product.

Temperature Dependence and Kinetics

The kinetics of the thermal decomposition of waste plastics and SAE 50 weight motor oil were conducted at 360, 370, 380, and 390°C (680, 698, 716, 734°F) and the masses of the products collected during these experiments are listed in Table 4. During these experiments the distillate product was collected in separate receivers over 15 minute time intervals. The data collected for the distillate production were fitted to the first order rate equation and the rate constants determined.

$$kt = \ln (a/(a-x)) \quad (1)$$

where k = rate constant

t = time

a = initial mass of reactants

x = mass of produced distillates

Table 4. Product Distribution as a Function of Temperature

Temperature (°C)	360	370	380	390
Distillate, g	19.3	27.3	49.3	95.1
Heavy Oil, g	311.2	305.1	282.7	236.1
Coke plus Gas, g	0.9	1.6	1.6	0.9
Recovered Plastics, g	25.5	24.1	20.4	22.2

The rate constants (k), constants of integration, the correlation coefficients (r^2), and the plastics conversion are listed in Table 5. The correlation coefficients range from 0.994 to 0.999, indicating an excellent fit of the data to the linear relationship

of the first order rate equation. Both the reaction rate and the plastics conversion increase with increased reaction temperature as expected. The kinetic parameters determined for these experiments were used in the Arrhenius equation to estimate the apparent activation energy and the frequency factor.

$$k' = A \exp \left(\frac{-E_a}{RT} \right) \quad (2)$$

where k' = rate constant

A = frequency factor

E_a = activation energy

R = Boltzmann constant

T = temperature

Table 5. First Order Rate Constants for Distillate Production

Temperature (°C)	360	370	380	390
k (g/min.)	0.0009	0.0016	0.0028	0.0062
Constant	0.00	0.01	0.01	0.01
Correlation Coefficient (r^2)	0.999	0.998	0.999	0.994
Plastics Conversion (wt%)	20.1	24.6	27.9	30.5

The results from the calculation using the Arrhenius equation are listed in Table 6. The apparent activation energy was determined to be 52.3 kcal/mole and the frequency factor to be 2.12×10^{15} /min. The correlation coefficient (r^2) for the relationship was determined to be 0.990, indicating a good fit of the data to the linear relationship of the Arrhenius equation. Comparison of these results with similar results from the thermal decomposition of polystyrene in the presence of a heavy oil at temperatures between 390 and 415°C (736 and 779°F) in the absence of an initiator such as PVC show good agreement (Marsh 1993). Marsh has reported an activation energy of 46 kcal/mole, which with the scatter in the data is comparable to that observed in our study. Considering the chemistry of thermal decomposition of polystyrene as compared to other plastics in the mixture used in this study, one would expect a lower activation energy for polystyrene (Guffey et al. 1991).

Table 6. The Apparent Activation Energy Using the Arrhenius Equation

Activation Energy (kcal/mole)	52.3
Frequency Factor (/min.)	2.12×10^{15}
Correlation Coefficient (r^2)	0.990

Effects of Heavy Oil/Plastics Mass Ratio

Dilution of the plastics with the heavy oil has the potential of effecting the activity of PVC because of the availability of the plastic. In addition, economic considerations regarding the amount of plastics that can be processed with a given feed rate of the heavy oil/plastics feedstock are of importance in defining the activity of PVC. Three experiments were performed to determine if changes in the heavy oil/plastics mass ratio have effects on plastics conversion. Three different heavy oil/plastics mass ratios were studied in experiments conducted at 380°C (716°F) with the addition of PVC. The heavy oil/plastics mass ratios studied were 21:1, 10:1, and 5:1. The results of these studies are listed in Table 7.

Examination of the results listed in Table 7 indicates the plastics conversion is highest at the higher dilutions (21:1 and 10:1) and decreases with decreasing dilution of the waste plastics. However, the total conversion shows an increase between heavy oil/plastics mass ratios of 21:1 and 10:1. The difference between the total conversion at 10:1 and 5:1 heavy oil/plastics mass ratios is not considered to be significant.

Table 7. Comparison of Plastics Conversion as a Function of the Heavy Oil/Plastics Mass Ratio

Heavy Oil/Plastics Ratio	21:1	10:1	5:1
Temperature, °C	380	380	380
Plastics Conversion (%)	28.5	27.9	22.4
Total Conversion (%)	12.3	14.0	13.8

The important point to note from these results is that the plastics conversion is higher at the higher plastics dilution (21:1). The optimum dilution cannot be determined from these experiments, and in addition to the technical considerations, economic factors will also effect the optimum dilution. Additional significance of these results will be discussed in a later section.

Effects of Different Heavy Oils

The type of oil used in the process was also evaluated to determine if it has an effect on the plastics conversion. A summary of the results from two experiments conducted with two different types of heavy oils are listed in Table 8. The residence time, temperature, and the heavy oil/plastics mass ratio were held constant between these two experiments.

Table 8. Comparison of Plastics Conversion Using Different Heavy Oils

Temperature (°C)	390	390
Heavy Oil	FCC ^a	SAE ^b
Plastics Conversion (%)	75.9	30.5

a FCC is fluidized bed catalytic cracker heavy recycle oil

b SAE is SAE 50 weight

Plastics conversion increased from 30.5% when SAE 50 weight oil was used to 75.9% when the heavy oil was fluidized catalytic cracker heavy recycle oil (FCC). The SAE 50 weight oil is composed of compounds that contain a high percentage of cyclic saturated compounds with alkyl substituents. These types of compounds are relatively reactive in free radical processes and will undergo decomposition in this process to produce a significant amount of distillate. The FCC heavy recycle oil has been thermally and catalytically stressed in the FCC process, resulting in an oil that is essentially devoid of cyclic saturate structures and alkyl substituents. This type of oil is not expected to be reactive in a free radical process. In addition, in earlier experiments using only the FCC heavy recycle oil without plastics, measurable quantities of distillate were not produced between temperatures of 390°C and 450°C (734 and 842°F) (Guffey et al. 1991). The importance of these results is that the type

of heavy oil used in the process will have a significant effect on the plastics conversion and distillate yield.

Theoretical and Actual Conversions

There appears to be a synergistic effect between the waste plastic and the heavy oil in the presence of PVC. Two experiments were performed at 390°C (734°F). One of the experiments did not use the plastics charge and was designed to determine the distillate yield from the oil. The second experiment was performed in the normal manner with the plastic and heavy oil charge. The results from these two experiments are listed in Table 9.

Table 9. Comparison of Experimental Distillate Yields at 390°C with Calculated Yields

Plastics Used	No	Yes	Yes
Result	Expt.	Expt.	Theo.
Plastics Conversion (%)	—	30.5	—
Total Conversion (%)	11.5	26.9	13.1

The total conversion to distillate for these experiments is 11.5% without plastics, and 27.0% with both plastics and heavy oil. Based on the total conversion (11.5%) from the experiment not using plastics and the plastics conversion for the experiment using plastics (30.5%), a theoretical recovery can be estimated. This calculation was performed to determine if the yield from coprocessing heavy oil and plastics is independent of the mixture. The calculation was performed by multiplying the weight fraction of the plastics conversion (30.5%) by the plastics charge (31.9g) and the weight fraction of heavy oil converted to distillate (11.5%) in the absence of a plastics charge by the heavy oil charge (319.6g). The two products were summed to provide an estimated yield. The theoretical conversion is calculated to be 13.1%. This value is significantly lower than the experimental conversion of 26.9%. These results indicate that there is a synergistic effect. Apparently the initiator, in combination with the plastics, enhances decomposition of the SAE 50 weight oil. This may have additional

economic importance in the processing of heavy oils, especially if one wishes to coprocess plastics with waste lube oil.

Reaction Model

The thermal decomposition technology for processing waste plastics is a relatively low-temperature process based on thermal decomposition of a mixture of waste plastic resin types in the presence of a low-value heavy oil. The results presented above demonstrate that the addition of PVC to the reaction promotes thermal decomposition of the plastics and in some cases the heavy oil. This enhancement is observed as an increase in distillate production and an increase in plastics conversion. Any mechanism proposed to explain the observed activity in the presence of PVC must be consistent with the results presented in this report. These results include:

1. The apparent activation energy calculated for this reaction is comparable to the activation energies reported for other thermal decomposition processes. It is not significantly lower as would be expected for a catalytic process.
2. The plastics conversion increases with increased dilution of the plastic in the heavy oil.
3. Different types of heavy oil undergo different degrees of thermal decomposition in the presence of PVC.

Thermal decomposition has been explained as a free radical process that requires sufficient energy being supplied to the system to cause breaking of covalent bonds to produce the free radicals (Rice and Herzfeld 1934). At the temperatures required to supply this energy, thermal decomposition reactions proceed to fragment or crack organic compounds into lower molecular weight species. The importance of free radicals in the thermal decomposition has been discussed with respect to liquefaction of coal and waste tires (Ibrahim and Seehra 1993). In their studies, Ibrahim and Seehra have shown there is a rapid formation of free radicals before the onset of thermal decomposition. They have postulated that a threshold level of free radicals is required to initiate thermal decomposition. In addition, free radical initiators have been used to promote processes based on free radical mechanisms (Scott

1972). This results in elimination of an induction period during which free radicals are formed.

We believe the mechanism for the reduction in the temperature required for thermal decomposition observed in our studies is based on a free radical initiator. Polyvinyl chloride has been shown to undergo thermal decomposition at 220°C (428°F) to yield hydrogen chloride and coke. The temperature at which most organic compounds begin to undergo thermal decomposition is around 400°C (752°F), and the temperature at which PVC begins to thermally decompose is significantly lower than would be expected. Since thermal decomposition of PVC proceeds by a free radical mechanism, it releases free radicals that can function as initiators for the thermal decomposition of the plastics and the heavy oil (if the mixture is of the right composition).

Using the free radical initiator concept as a basis, the following mechanism can be proposed. The free radicals liberated from the PVC (or any other compound that will undergo thermal decomposition) at temperatures below about 400°C (752°C) act to start the process. In the reaction media, decomposition of the initiator produces free radicals at a rapid rate, reducing the induction period. The free radicals attack the polymer structures to satisfy their electronic structures. This results in the abstraction of a proton from the polymer molecule, which initiates the free radical process to decompose the polymer structure. In the case of PVC as the free radical source, the free radicals formed will be hydrogen and chloride radicals. When these free radicals abstract protons from the polymeric structure, the products will be hydrogen gas and hydrogen chloride, as well as polymer free radicals.

Once a radical is formed in the polymeric structure, the polymer will undergo depolymerization reactions following a chain reaction mechanism as proposed by Rice and Herzfeld (1934). This reaction will proceed through fragmentation reactions followed by rearrangements of the fragments to produce stable cyclic and olefinic species. The result is decomposition of the plastics at temperatures lower than expected, providing products that are low molecular weight hydrocarbons in the gasoline and diesel fuel boiling range.

The results from the studies evaluating the effects of diluting the plastics with heavy oil are consistent with this model and may be one of the more important

variables in the commercialization of this concept. The heavy oil functions as both a heat transfer medium and as a diluent for the plastics. In the function of a diluent, the heavy oil will act to isolate different plastic molecules from one another. In this manner, radicals formed in the polymer chains will not be able to contact one another to react. This will decrease the tendency for these interactions to result in chain reaction termination reactions and thus allow depolymerization. The type of heavy oil used will affect the reaction by providing a termination reaction step or by providing an additional reaction pathway (thermal decomposition of the heavy oil).

For this reason, selection of the heavy oil is important. The results discussed above show there is higher plastics conversion when FCC heavy recycle oil is used in place of SAE 50 weight oil. The FCC heavy recycle oil is quite refractory compared to the SAE 50 weight oil. Therefore, interactions between the polymer radical and the FCC heavy recycle oil are not expected to result in termination reactions. On the other hand, SAE 50 weight oil is more reactive. Interactions of the heavy oil with the polymer radicals will result in providing additional reaction pathways via thermal decomposition of the heavy oil. This will increase distillate production as was observed in the experiment using SAE 50 weight oil. The results from this study support this mechanism.

The kinetics of this reaction are important, and the calculated activation energy is comparable to the activation energy determined for many thermal decomposition processes. If the model for this reaction were to be based on a catalytic activity of PVC, then one would expect the apparent activation energy to be substantially lower. However, the proposed model (based on PVC functioning as a free radical initiator) is consistent with the apparent activation energy. The free-radical initiator serves to generate the free radicals very rapidly. This reduces the induction period at a lower-than-expected temperature and allows free radical attack of the polymer structure. The rate limiting step in the reaction is not the initiation of the radical, but the production of thermal decomposition products collected as distillate. Therefore, changing the mode of forming free radicals in the polymer structure from a thermal process to a free-radical initiator process would not be expected to affect the apparent activation energy.

A major key to this waste plastics conversion concept is the use of the decomposition initiator in the heavy oil/plastics media. For this concept, the free-

radical initiator can be any compound that will form free radicals at temperatures below about 400°C (752°F). The heavy oil acts as a heat transfer medium and a diluent that isolates the radicals in the polymer structures. Selection of the heavy oil is an important consideration because reactive oils will act as scavengers and partially terminate the free radical process.

CONCLUSIONS

This investigation was undertaken to evaluate the observed reduction in the thermal decomposition temperature when waste plastics are coprocessed with a heavy oil. Based on the results of this investigation, the following conclusions can be made.

1. The component in the reaction matrix responsible for the observed reduction in the thermal decomposition temperature is polyvinyl chloride.
2. Higher plastic conversions are obtained with more dilute solutions of plastics in the heavy oil.
3. Heavy oils such as fluidized-bed catalytic cracker heavy recycle oil promote the plastics conversion to a greater extent than more aliphatic oils such as SAE 50 weight motor oil.
4. The mode of action of polyvinyl chloride in reducing the reaction temperature for thermal decomposition of waste plastics appears to be that of a free radical initiator, which reduces the induction period for the formation of free radicals at the lower temperature.

DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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