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LOW TEMPERATURE OXIDATION OF USED LUBRICATING OIL

Masters Thesis (M.Eng.)

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ABSTRACT

In order to deal with the negative impacts associated with disposal of used oils by thermal remediation, a study of the material under combustion-like conditions was undertaken. Two used motor oils were subjected to slow heating using a Thermogravimetric Analyzer coupled with a Fourier Transform Infrared Spectrometer. Based on the results obtained, mechanisms of the general transformation process the oil undergoes and the evolution of the solid particles were proposed. The presence of Polycyclic Aromatic Hydrocarbons (PAHs), considered hazardous, was observed and individual PAHs were identified. The results show that initial oxygen content in the oil plays a significant role in the thermal remediation process, primarily leading to smaller, more compact final residues. This may have significant implications in terms of leachability of toxic metals. The insight gained here can be utilized in further studies to understand and then possibly control, the process in practical combustion systems.

RÉSUMÉ

La déstruction des huiles usagées par procédés thermiques sont nocives. Pour résoudre ce problème, une étude préliminaire sur un procédé de quasi-combustion a été entamée. Deux huiles pour moteurs ont été chauffées en présence d'un analyseur thermogravimétrique avec infrarouge. La transformation de l'huile au cours du chauffage a été étudiée suivant plusieurs paramètres pour comprendre les changements physiques et chimiques au coeur de l'échantillon.

Un méchanisme du procédé a été réalisé. Les résultats obtenus dans cet étude préliminaire démontrent que le taux d'oxygène initial dans l'huile joue un rôle important dans le procédé, principalement en reduisant la quantité et grandeur du résidu final. Cela pourrait avoir des répercussions significatives dans la lixiviation des métaux toxiques. La présence d' Hydrocarbures Aromatiques Polycyclés a été aussi déterminée. Les informations obtenues dans cette étude peuvent être utilisées pour mieux comprendre et eventuellement mieux contrôler les méthodes thermiques qui utilisent les huiles usagées.

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Chapter 1: Review of Pertinent Subjects

1.1 Waste Generation

Waste generation is not a new phenomenon. However, the disposal of the waste material in a safe and economical way is becoming increasingly difficult. Through a combination of government regulations, economic constraints and public outcry, many of the disposal techniques previously used have been or will need to be abandoned or improved. New disposal methods are therefore required to alleviate the problems now being faced in the waste disposal industry. These new methods are being met with greater scrutiny from both government and the public in general and thus, must be proven to address environmental concerns. It is therefore necessary to research areas of waste disposal in more depth so as to be able to understand the processes taking place and be able to justify and validate any new disposal methods.

Waste material can be defined as an undesirable by-product generated during a process leading to a desired product or use. This waste could be in either the gas, liquid or solid phase, or a combination of the three. Although each type of waste has specific concerns associated with it, the work undertaken here concentrates on liquid wastes. There are a variety of liquid wastes, each being important in terms of environmental considerations.

1.2 Liquid Waste Overview

Liquid wastes that are generated can be of different types and classified as water, oil and other organic material. A general overview of the project justification is given in Figure 1.1 (a more detailed justification follows). This research concentrates on oil wastes which can be defined, in general, as oil that remains once the original material can no longer be used for the purposes originally required of it due to either trace impurities or loss of properties. Waste oils can be generated from many different sources such as spent lubricants as well as others, such as use in electric transformers. These waste oils account for a significant amount of waste material which need to be disposed of in a manner that is both economically and environmentally acceptable.

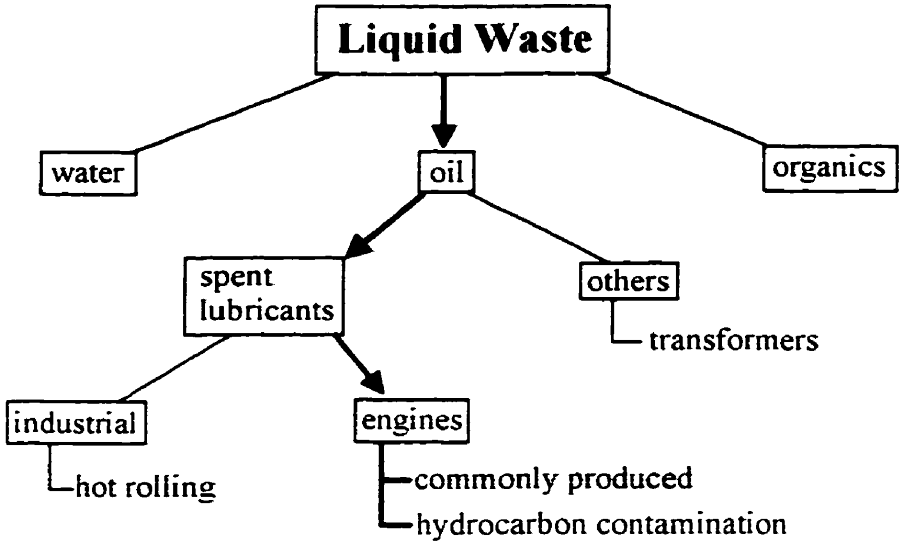


Figure 1.1: Liquid Waste Overview

The present work concentrates on a specific type of waste oil, spent lubricants, which can come from industrial processes such as hot rolling in metallurgical processing as well as from the use in engines as lubrication. One of the more common and significant sources arises from the use of engine lubricants in automobiles. Waste oil generated from automobile usage is the type of material studied in this work due to its constant generation from routine oil changes, as well as the potential for hydrocarbon contamination from the fuel used in the vehicle, which would complicate disposal of this material.

1.3 Used Oil

The numerous sources of used oil generators can be classified by the fluid function and are shown in Table 1.1 with examples of sources for each. The classification falls into four categories: lubricating oils, hydraulic fluids, metal working fluids and insulating fluids (or coolants). The bulk properties of these oils will be similar. However, the virgin oils in each category have their own quality requirements, according to their specific use. These requirements, together with the fact that the uses themselves are different, means that the used oils generated from each source are likely to have some differences in chemical and physical properties (at least with respect to trace compounds). These differences may be important in terms of disposal method selection.

Table 1.1: Waste Oil Sources [1]

Classification	Sources
lubricating oils	engine, turbine, gear
hydraulic fluids	transmission fluids
metal working fluids	cutting, grinding, machining, rolling, stamping, quenching, cooling oils
insulating fluid/coolant	transformer oil

Prior to discussing the different used oil disposal methods available, it is important to mention general properties and characteristics of this material that will affect appropriate selection. Waste oils originating from different sources typically end up in collection centers. Therefore, contaminant concentrations will vary from center to center and thus, characterization of waste oils represent typical averages. (For example, the waste oil from one car is not necessarily exactly the same as that from another and when mixed with waste from other sources, can lead to a used oil having atypical properties.)

In general, used oils have properties comparable to heavy fuel oils except for density and trace contaminants. This is especially true in terms of heating value, where waste oils have heating values typically greater than 35 MJ/kg (15000 BTU/lb). Also, used oils generally have less sulfur than heavy fuel oils which means, for example, that using waste oils as a supplemental fuel would generally reduce SO_x emissions[2] and therefore be advantageous.

When compared to the virgin oil, however, used oils will usually contain some trace impurities such as: suspended metal particles, dirt, water, and halogenated solvents. Waste oils will also differ from the original oil in some other physical properties resulting from its usage (e.g. viscosity and flash point may change from virgin grade to waste oil). A partial list of the contaminants found in waste oil is given in Table 1.2, which shows the approximate concentration range as well as the potential source of these contaminants. All of these contaminants need to be addressed when dealing with disposal of waste oils.

1.4 Waste Lubricating Oils

The oil being studied is a waste lubricating oil and, as mentioned previously, the makeup of the original oil is important. Lubricating oils, in general, are composed of an organic (or petroleum) base. A break-down of the hydrocarbon types typically found in

Table 1.2: Contaminants of Potential Concern in Waste Oils[3]

Organic contaminants	Probable Source	Approximate conc range, µg/L
Aromatic hydrocarbons	Petroleum base stock	
Polycyclic (PAH)	or contamination	
benzo[a]pyrene		360-62,000
benz[a]anthracene		870-30,000
pyrene		1,670-33,000
Monoaromatic		
alkyl benzenes		900,000
Diaromatic		
naphthalenes		440,000
Chlorinated hydrocarbons	May be formed chemically	
trichloroethanes	during use	18-1,8000
trichloroethylenes		18-2,600
Metals	Additive package,	
barium	Engine/ metal wear	60-690
zinc		630-2,500
chromium		5-24

lubricating oils is shown in Table 1.3. Generally, lubricating oils have carbon content originating mainly from paraffinic hydrocarbons (~70%), although a small portion (<5%) is found in aromatic chains (which is a concern to be discussed later). The hydrocarbons are composed mainly of those having an approximate molecular weight in the order of 420-520 a.m.u. and a boiling point of 350-450°C, depending on the grade of oil[4].

Table 1.3: Typical Lubricating Oil Composition [4]

C in paraffinic chains	65-75%
C in naphthenic chains	20-30%
C in aromatic rings	< 5%

Additives are added to the base oil in trace amounts, depending on its use, to improve the characteristics and the life of the oil. The additives consist of inorganic material such as sulfur, nitrogen and metals (e.g. barium, zinc and chromium) and can account for up to 15% of the oil by volume[5]. Therefore, these constituents also need to be accounted for when considering the treatment method of the waste material.

The research concentrates on waste lubricating oils from a particular source, namely automobiles. This is because one of the more common sources of used oil is lubricating oil from vehicle maintenance (i.e. waste crankcase oils or WCOs) due to the high number of vehicles in use[5]. WCOs are removed from the crankcase of internal combustion engines after a period of usage when its properties are no longer suitable. Table 1.4 shows a typical make-up of waste crankcase oils from the automotive industry.

Table 1.4: Composition of WCO [6]

Parameter	Value
Specific gravity, API	24.6
Viscosity (310K)	53.3 centistokes
Flash Point	102°C
Water	4.4% vol
Sulfur	0.34% wt
Ash	1.18% wt
Lead	1.11% wt
Calcium	0.17% wt
Zinc	0.08% wt
Phosphorous	0.09% wt
Barium	568 ppm
Iron	356 ppm
Vanadium	5 ppm

In Canada, in 1990, the volume of recoverable WCO needing disposal was estimated to be $227.3\text{x}10^6$ L (which works out to about 56% of the $413.3\text{x}10^6$ L of crankcase oils sold in the automotive industry in that year). The remainder of the oil was consumed during engine use (either due to burning and subsequent escape through the exhaust or through leakage)[5]. (Waste disposal research can only deal with used oil that can be collected; however, the portion of oil that is lost during use is very significant in contributing to detrimental effects on the environment and is worth further study as well.)

By comparison, in the United States, the problem is much greater due to the greater amount of vehicles in use. It is estimated that $5216\text{x}10^6$ L (1.378 billion gallons) of automotive waste oils are generated per year, with about half coming from people who change the oil on their own vehicles (known as Do-It-Yourselfers, or DIYs). In addition to the amount collected above, between $731\text{-}1514\text{x}10^6$ L (193-400 million gallons) are released into the environment (e.g., through dumping) by DIYs[7], which is greater than the amount collected in Canada. When the amount of WCO produced in Canada and the United States is considered, this source of waste material becomes a very significant one and thus requires attention in terms of implementing acceptable disposal techniques.

1.5 Disposal Methods

Due to increasing limitations on disposal methods (through regulations and public relations issues), the primary goal in waste disposal should be to attempt to minimize the amount of waste generated by either altering the generating process or improving the longevity of the oil through changes in its physical and/or chemical properties. However, despite waste minimization attempts, used oil is unavoidably produced and thus still requires treatment and disposal. (For the purposes of this study, waste oil minimization techniques will not be considered in order to focus on the waste after it is generated.)

In order to properly implement a used oil disposal method, it is essential to establish an efficient collection method in order to help make treatment alternatives more economically feasible, particularly in the case of the small generator. It is often during this collection process that the waste oil is contaminated with such things as chlorinated solvents which seriously alter the effectiveness of a disposal method.

The ultimate goal of waste oil treatment is to render the material that is disposed harmless to the environment or at least minimize the release of toxic compounds. There are several disposal methods that can be applied to deal with the waste material. The more common alternatives for general waste disposal are found in Figure 1.2, together with some of the selection criteria. There are biological and chemical treatment methods which involve the removal of undesired contaminants through the addition of microbes and chemicals, respectively. These methods can be generally time consuming or expensive. Other alternatives include recycling and landfilling which are at opposite ends of what is desirable from an environmental point of view. Recycling saves natural resources but is costly while landfilling is usually cheap but detrimental to the environment. Another option, thermal remediation, is the method of interest in this work, and involves heating the waste and extracting a portion of the energy available from the waste. Finally, the waste can be subjected to combinations of these treatment methods.

The alternative disposal method selected is based primarily on the properties of the waste material and on economics of the process. The choice may also be influenced by the potential for future liability to the generator as well as on environmental concerns, either from a public relations or a regulatory point of view.

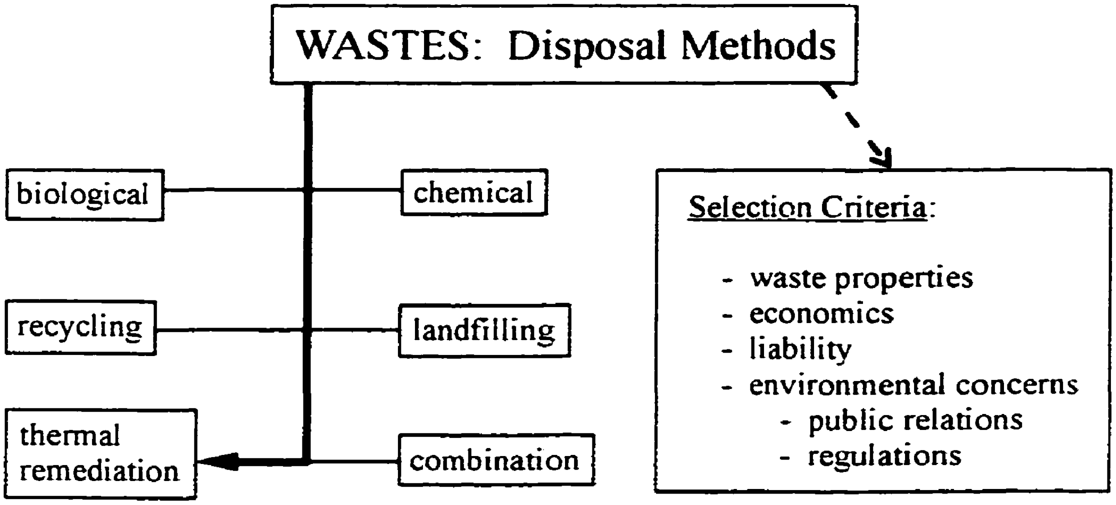


Figure 1.2: Waste Disposal Methods

The disposal methods available to deal with waste oils specifically are similar to those mentioned above. Some of the options previously utilized to deal with waste oil, such as indiscriminate dumping, landfilling and land disposal, have been generally accepted and therefore utilized with little concern. However, as environmental concerns grow and more stringent controls are being placed upon industry, such methods are no longer acceptable and should be minimized in favor of other disposal techniques since the above options prevent the oil from being treated. Other options, such as thermal remediation and recycling, are more attractive and more favorable, especially if some of the environmental concerns associated with them could be addressed, which is precisely one of the long term objectives of this work.

The three main disposal methods that are favorable in dealing with waste oils are: recycling, re-refining, and use as a fuel (thermal remediation techniques). These methods are discussed in the following sections. Each of these methods have their benefits as well as their disadvantages that need consideration when selecting a treatment method.

One of the alternative disposal methods to deal with used oil is to recycle and re-use the oil. The processes involved in recycling and re-refining are similar and are therefore discussed together. There are different levels of recycling. Recycling waste oil involves subjecting the oil to a process such as a physical treatment which may result in oil with lesser quality than the original oil. The recycled oil can therefore be re-used in a less demanding application without requiring further treatment.

Physical treatment of waste oil involves removal of solid contaminants. Methods such as settling, filtration and dehydration are used but these do not remove all of the solid material such as trace metals because of their small particle sizes. These methods are relatively simple and therefore have lower costs than more elaborate methods such as centrifugation, clay contacting and distillation. Although these methods are more effective, their extra cost sometimes makes the recycling and re-refining processes economically unfeasible and are therefore, not usually utilized.

Alternatively, the oil can be further treated to produce a fuel grade oil and then subjected to thermal remediation (which is discussed later). [Note that in the case of waste oils, recycling is often a precursor to other treatment methods such as for use as a fuel.] The waste can also be treated prior to submitting it to a refining process. Re-refining waste oil involves using the material in a refining process to produce an oil having properties that meet virgin product grade specifications (or another finished product such as gasoline). In Canada, there were nine re-refining operations in use in 1993[5].

Although, from an environmental point of view, recycling and re-refining seem ideal, the stringent specifications of the finished product, as well as the inconsistencies in waste oil makeup, do not always make this option economically or technologically viable. In addition, the re-refining process also generates pollutants in the form of air emissions, liquid effluent and solid wastes that will have to also be dealt with[5]. These concerns sometimes limit the use of this alternative.

1.6 Thermal Remediation

The last main disposal method for waste oils involves thermal remediation. Some of the more attractive alternatives are those involving thermal remediation of the waste material which explains why addressing the concerns associated with these methods is important. Thermal remediation is a very attractive disposal method for a number of reasons and an explanation of thermal remediation is given in Figure 1.3.

Thermal remediation involves application of high temperatures to the waste in order to extract part of the energy available from the waste. At the same time, the contaminants in the waste can be destroyed. The advantages of such methods are the

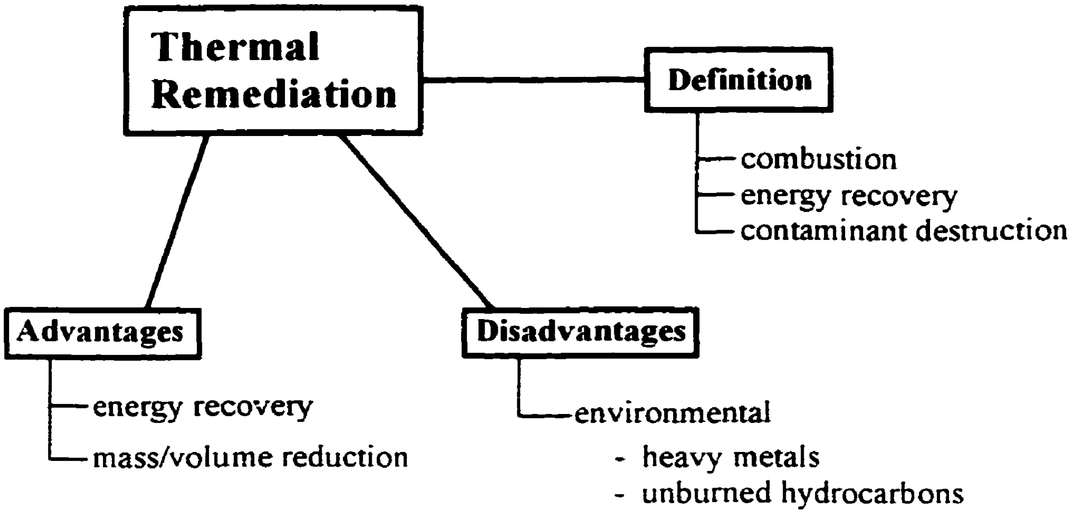


Figure 1.3: Thermal Remediation

immediate reduction of both the mass and volume of material needing ultimate disposal. This reduces the generator's storage and handling costs of the waste material. In addition, the energy extracted from the waste can be used in producing utilities, such as steam or electricity. Through these heat recovery techniques, the operating cost of the process can be reduced by the use on site or the sale of the utilities generated. Therefore, from an economic point of view, thermal remediation methods are generally quite advantageous. Furthermore, since there already exist several processes that currently use virgin fuel oil (e.g. utility boilers), supplementing the virgin fuel by used oil would be beneficial and would not require excess capital investment. Unfortunately, most combustion methods are not as attractive from an environmental point of view. Typical processes involve the release of unwanted emissions such as unburned hydrocarbons as well as the emissions of heavy metals which are detrimental to human health and thus, need to be minimized.

The current research involves the combustion of waste lubricating oils because they are good candidates for thermal remediation. What makes waste lubricating oil particularly attractive to thermal remediation results from some of its properties. Waste lubricating oil has a high heating value, over 37 MJ/kg (16000 BTU/lb) which is comparable to that of heavy fuel oil at 42 MJ/kg (18000 BTU/lb). This means that a relatively high amount of energy can be extracted from the use of waste lubricating oil in existing processes that currently use heavy fuel oils. Another interesting property is the low ash percentage of waste lubricating oil. Since everything but the inorganic material in the oil can burn, the low ash percentage significantly reduces the amount of waste needing ultimate disposal. This will significantly reduce the disposal cost to the generator of the waste since only the inorganic material will need disposal after treatment.

However, there are environmental concerns associated with combining thermal remediation and waste oils. These concerns are summarized in Figure 1.4 and result from the emission of toxic material that may be present in the oil. (Note that the arrows in the figure point to areas of concern in this study.) These emissions can be in the gas phase, as products of incomplete combustion, or as the solid particulates that result during the process. The major differences between virgin fuel and waste oil are in the levels of the contaminants and therefore, the concern associated with burning waste oil comes from their release. Some of the contaminants are considered toxic and can make their way into the environment through air emissions, fly ash or bottom ash emissions. These materials include PCBs, heavy metals, unburned hydrocarbons, organochlorines and solid particulates which all have negative impacts on the environment and need to be minimized.

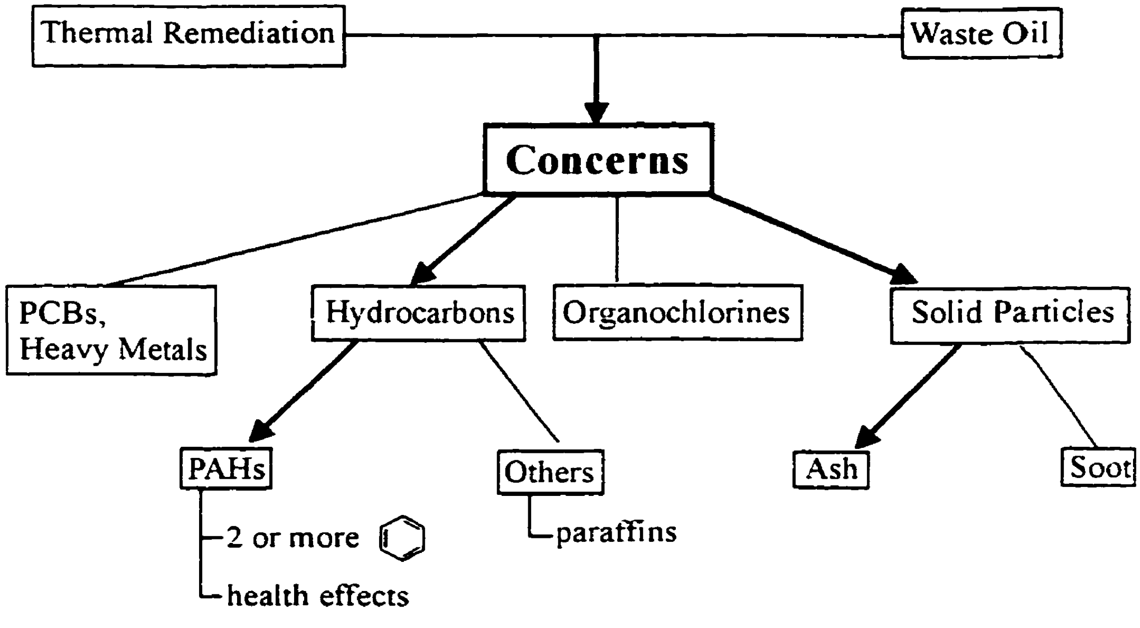


Figure 1.4: Concerns Particular to Thermal Remediation of Waste Oils

Organochlorines are hydrocarbons that contain halogenated compounds (e.g., chlorine). They may result from the reaction of hydrocarbons with halogenated compounds during the use of the oil. Since virgin oil typically contains little of halogenated compounds (< 100 mg/kg), it is more likely that these contaminants are a result of mixing other wastes with the oil during storage[8].

Trace heavy metals are either introduced to the oil as part of the additive package (i.e. prior to use) or may be a result of wear from the instrument/device that uses the oil (such as an engine). Metals such as zinc, chromium and lead are among the metals of concern due to the potential negative effects from exposure to these compounds. Also, metals are known to act as catalysts for hydrocarbon oxidation and thus their presence may affect the combustion process.[9]

Solid particulates are also a concern when discussing thermal remediation of waste oil. Solid particulates, which include ash and soot, may contain some hazardous compounds, such as toxic metals. Other emission concerns from thermal remediation of waste oils can come during the cleaning and maintenance of the equipment used in the combustion process (and are similar to those described above), as well as NO_x and SO_x that are generated during the process. However, for WCOs in Canada in 1990, the estimated emissions from combustion processes of NO_x and SO_x was as follows[5]:

NO_x	174.5 tonnes/yr
SO_x	569.3 tonnes/yr

In comparison to other sources in Canada, the following emissions are typical:

NO_x from transportation sector	1 180 000 tonnes/yr
SO_x from a major Canadian industrial plant	695 000 tonnes/yr

Since these levels are much higher than those released through the burning of WCOs, the contribution of NO_x and SO_x levels through the burning of WCOs is not a major concern.

Hydrocarbons are of particular concern since oil comprises mainly of a mixture of hydrocarbons which, if not burned completely, will be released into the atmosphere. The hydrocarbons present in waste oil that are of most concern are a particular class of aromatic hydrocarbons known as Polycyclic Aromatic Hydrocarbons, or PAHs[5]. PAHs are those hydrocarbons containing 2 or more benzene rings. Some of these hydrocarbons are particularly toxic, such as benzo(a)pyrene, and they can be found in varying amounts in waste oil, depending on the source of the oil.[5] These PAHs may also come from contamination by external sources or they can be produced during the use of the oil[8].

Since some of these compounds have been found to be carcinogenic and mutagenic, their release into the atmosphere is a problem.

In general, the emission levels of these contaminants are low and vary according to the composition of the feed and the type of combustion unit. However, constant operation may cause significant accumulation of these pollutants over time. For the example of PAHs, although emitted in trace amounts, constant exposure to even small levels may be a concern due to some of these compounds being mutagenic and carcinogenic.

One of the reasons to study behavior of waste oil during thermal remediation is the current existence of a number of thermal remediation processes in which waste oil can be burned as a fuel, and in some cases, are currently being used. For example, processes such as electric utility boilers, cement kilns, and industrial boilers are potential users of waste oil. In essence, the waste oil can be used as a fuel (or as a supplemental fuel) in a process such as a boiler that produces steam, since it is more economical to use waste oil instead of having to purchase as much virgin fuel oil. In order to promote the usage of combustion methods for the disposal of used oils, it is necessary to improve the process from an environmental point of view to deal with the different areas of concern.

One of the thermal remediation methods available is to burn the waste oil in either a commercial or industrial boiler. Waste oil can be used as the primary fuel in a commercial boiler or as a supplemental fuel in the larger industrial boilers and furnaces. The commercial boiler is rated at a heat capacity of less than 3 MW (10×10^6 BTU/h) and is of concern more than the other methods due to the shear number being used[8]. Also, these units typically have low stack heights (<12 m) which puts hazardous emissions closer to the general population[8]. Commercial boilers are used generally to heat apartment buildings, greenhouses, and small institutional facilities such as schools and hospitals. Typical combustion efficiencies of commercial boilers are >99.9%[8].

Industrial boilers are utility or power generating boilers used to provide hot water or steam for manufacturing processes. These are generally rated at >7 MW ($>25\times10^6$ BTU/h) and usually use a blend of recycled oil and virgin fuel oil, to ensure a constant supply[8]. Typically, industrial boilers can be equipped with better air pollution control equipment to deal with some of the emissions problems associated with the process.

Space heaters can also use waste oil for fuel. These are typically sold to service stations and maintenance shops of firms with several of their own vehicles. These are meant to be used on site by the generators of waste oil. They tend to have small heat capacity, <0.15 MW (<$0.5 x 10^6$ BTU/h) and use 3.8-7.6 L/h of used oil[8].

Regulations exist which govern the use of waste oils as fuel. In order to use waste oil as a fuel without the need for additional permits, the oil must meet certain criteria for a specification fuel. These criteria are listed in Table 1.5 and are the criteria that apply in the United States (the Quebec criteria, where different, are given in parentheses).

Table 1.5: Fuel Specifications[6] (Quebec[10])

Fuel Designation	Variable
On-Specification	metal content (maximum)
	arsenic, 5 ppm
	cadmium, 2 ppm
	chromium, 10 ppm
	lead, 100 ppm
	flash point (minimum), 38°C
	total halogens (maximum), 1000 ppm (1500 ppm)
Hazardous Waste	total halogens, 4000 ppm or greater (N/A)

If the oil does not meet these criteria, it is considered either an off-specification fuel (if the halogen content is less than 4000 ppm) or a hazardous waste (if the halogen content is 4000 ppm or greater). In the United States, waste oils that are classified as on-specification can be burned in most facilities as long as air emission standards are met. Off-specification fuels can be used as long as it can be shown that it was not mixed with an otherwise hazardous waste. Due to this criteria for total halogens, it is essential to keep the waste oil collected away from possible contamination from halogenated solvents. Hazardous waste oils can be burned if a special permit is issued guaranteeing a more efficiently operated process[6]. Sometimes, in order to burn a fuel that meets the above specification, used oil can be blended with virgin fuel to lower the contamination levels.

When burning waste oils in industrial boilers, for example, it is also important that the burner be designed to deal with the possibility of low flash point material. The oil may be contaminated with solvents such as acetone and benzene that may cause the material to ignite at lower temperatures and thus run the risk of explosion. If the burner is properly designed then the waste can be fired with less concern for explosion[6].

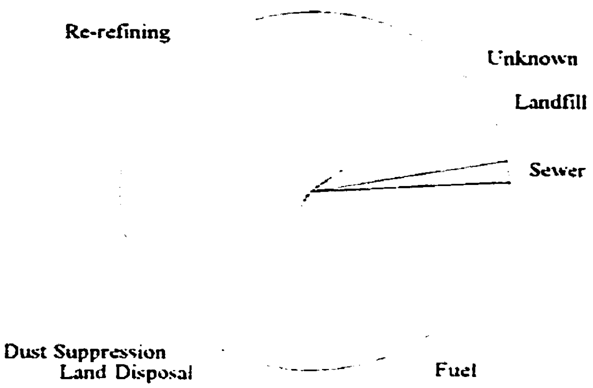
1.7 Current Disposal Practice Of Waste Lubricating Oil

Information on waste oil disposal is not very easy to quantify. (For example, someone who throws oil in a ditch is not apt to tell anyone about it.) For that reason, most of the numbers available are estimates but are still useful in getting a sense of the magnitude of the problem. In the United States, about 70% of all the liquid and solid hazardous wastes commercially incinerated are being burned in cement kilns[11]. The cement industry requires a significant amount of fuel and it is more economical to use cheaper sources of fuel to be burned in conjunction with the primary coal fuel[12]. (This makes this industry a good candidate for using waste lubricating oils as a fuel.) In the case of oils specifically, in 1983, in the United States, it was estimated that $1514\text{x}10^6$ L of used oil was disposed as waste through landfilling, incineration or dumping[6].

Since the oil being studied in this research is waste lubricating motor oil, i.e. WCO, it is of interest to look more closely at the trend in disposal of this type of waste. There was an in-depth study done concerning the fate of these oils generated in Canada in 1990 and a summary of the results is shown in Figure 1.5. As can be seen, 50.5% by volume of WCOs were re-refined and 33.3% were used as fuel. The remainder of the WCO was disposed in sewers, landfills, through land disposal (i.e. municipal waste) and dust suppression (on dirt roads). Of the WCOs used as fuel (i.e. $77\text{x}10^6$ L), $70.5\text{x}10^6$ L (91.6%) were used in boilers, $4.8\text{x}10^6$ L (6.2%) were used in space heaters and $1.7\text{x}10^6$ L (2.2%) were used as a fuel in diesel engines[5].

This data shows that there is significant amounts of used motor oil currently being burned in Canada. Due to the concerns associated with the combustion process previously described, the need for more efficient and less hazardous combustion units is clear. Methods such as landfilling and indiscriminant dumping should be discouraged in favor of thermal treatment and recycling/re-refining methods. In other words, it would be beneficial to increase the use of more desirable methods such as thermal treatment and recycling in order to decrease the use of the less desirable methods. However, since these methods, still add significantly to environmental concerns, research is required to improve them. Specifically, in the case of waste oil thermal treatment, the solid particle, metal, PAH and organochlorine behaviors need to be better understood so that design

Figure 1.5: WCO Fate in Canada, 1990 [5]



Source	Amount (L)	%
Re-refining	116×10^6	50.5
Fuel	77×10^6	33.6
Landfill	16.5×10^6	7.2
Dust Suppression	6.8×10^6	3.0
Land Disposal	6.4×10^6	2.8
Sewers	4×10^6	1.7
Unknown	2.8×10^6	1.2

improvements can be made to the combustion process. Prior to being able to improve the design of combustion units, a better understanding of pollutant behavior during the combustion process is necessary. To this end, the work being done here attempts to initiate that type of study.

Chapter 2: Purpose of Research

The combustion of waste lubricating oil is an attractive disposal method since the volume and mass of the waste requiring disposal is drastically reduced in addition to achieving some energy recovery. As environmental regulations become more severe, a better control of combustion systems is important in order to reduce the negative impacts. This can be achieved by determining the parameters in the combustion process which influence the formation and release of toxic by-products. In order to do so, one must first understand the fundamental behavior of the material (i.e., used motor oil) in this type of process. Once this fundamental understanding is achieved, one can then attempt to determine the important operating parameters in a combustion system that affect the different areas of concern. Only then can the environmental aspects of combustion be properly addressed so that a more controlled and environmentally acceptable combustion method can be ultimately proposed that would minimize environmental concerns. These concerns include: release of toxic species such as polycyclic aromatic hydrocarbons, and safe disposal of resultant ash, which may contain heavy metals.

The purpose of the current research is to perform an initial investigation into the behavior of waste motor oil combustion by observing the behavior of two such oils (Oil 1 and Oil 2) under the same experimental conditions. It was decided to subject two different used motor oils to the same conditions. Once the two oils were analyzed for some basic physical and chemical properties, it would be possible to attribute any differences in the process behaviors of the two oils to differences in properties (e.g., how water content may affect the process). With these observations, it was hoped to gain insight into the overall processes taking place.

Since combustion processes are inherently fast and exothermic, it was deemed necessary to slow down the process in order to make preliminary observations and maintain a uniform temperature throughout the sample[9]. Otherwise, observations on the changes the oil undergoes during the process would not be possible (or at least be quite limited) due to the short times involved. Therefore, it was necessary to slow down the process by subjecting the oils to a combustion-like process where, instead of bulk volume combustion, the sample undergoes surface layer combustion. This is because the sample container is only open from the top and thus, reaction gas access to the sample is limited to the top layers of the sample. Although a slowed-down process will not behave exactly like an actual process, it will allow the observer to distinguish between different events taking place during the temperature history since the slower heating rate will allow the temperature in the entire sample to be more uniform.[9]

Once the slow process is well understood, the process rate can be increased incrementally and observations compared to the original process. Eventually, the process rate will attain actual combustion rates and this process can be studied in comparison to the previous studies, in order to circumvent the difficulties that the speed of the process would otherwise have on observations. When the general process is understood, environmental aspects can be studied as well, using the same methodology. Since, in general, combustion processes involving waste oils are not usually operated above 1000°C, it was decided to study only a low temperature process, ending at 1000°C.

A low temperature process is appropriate in this type of study. Since the heating rate is slow, it is likely that the entire oxidation process will be over by 1000°C; the oil will have sufficient time to oxidize at the lower temperatures. In addition, a low temperature process will reduce NO_x formation from the air used as a reaction gas since thermal NO_x is only formed at higher temperatures. Another reason for applying a low temperature is that used oil has a high heating value which will allow for the recovery of energy without having to heat the material to as high a temperature, which lowers operating costs of the process. Similarly, the low ash content of used oil will mean that a high temperature will not be necessary to attain the reduction in waste mass and volume desired. Finally, in terms of soot formation during the combustion process, the low temperature results in a smaller amount of soot formation which is often associated with toxic compounds.

Different aspects of the process were investigated. These included:

1. Sample weight:
    - The weight behaviors were monitored using the thermogravimetric balance. This gave continuous information on the weight changes that the samples underwent, which were associated to the events taking place during the heating

and oxidation processes. The data acquisition system allowed for the correlation of weight reading to run time and furnace temperature so that analysis was facilitated. This gave a physical indication of overall process rates at different temperatures and allowed for inferences into the events taking place.

2. Gas-phase release:
    - Using the Fourier Transform Infrared Spectrometer (FTIR), it is possible to continuously monitor the chemical composition of the gases released during the process. Specifically, the evolution of typical combustion gases would help explain the physical and chemical changes the samples underwent.[9] Carbon dioxide, carbon monoxide and hydrocarbons were studied. The data acquisition system allowed for the compositional information to be correlated to run time and furnace temperature. In addition to these, the FTIR data was correlated to sample weight and percent sample weight remaining. Overall, the FTIR information provided an avenue to explain the chemical changes that the samples underwent during the heating process.
3. Solid-phase evolution:
    - After the original liquid oil was transformed into a solid, the morphological evolution of the residues generated was monitored to explain the processes involved in formation of the final disposed material. This was accomplished by collecting solid samples at different temperatures (i.e. stopping the heating process at a desired temperature and collecting a solid sample) and viewing the morphology of the solids using a Scanning Electron Microscope (SEM).
4. Polycyclic Aromatic Hydrocarbons:
    - The behavior of PAHs on a 5000 ppm naphthalene and benzo(a)pyrene spiked sample was studied to formulate some hypotheses about the behavior of these very important compounds during the process. This was achieved by comparing the behavior of the spiked sample to that of the unspiked sample to isolate the effects of the added hydrocarbons.

Chapter 3: Instrumentation

3.1 Research Instrumentation

The main instrumentation used in this research to study the behavior of waste oil is a combination Thermogravimetric Analyzer (TGA) and Fourier Transform Infrared Spectrometer (FTIR). The two instruments are connected via gas sampling accessories which allow the two to be used simultaneously. A Data Acquisition System (DAS) is utilized to control both of the instruments and make data interpretation compatible. A schematic of the instrumentation is shown in Figure 3.1.

3.1.1 Thermogravimetric Analyzer (TGA):

In order to control the rate of the combustion process to be studied in the manner that is desired and make observations on the process simultaneously, a thermogravimetric analyzer (TGA) was utilized. The TGA was used to simulate the temperature history, the residence time and the chemical environment of a waste oil in a practical thermal treatment unit. A schematic representation of the TGA is included in Figure 3.1. The TGA consists of an electronic recording balance and a furnace in which a sample is subjected to a programmed heating profile and its weight change continuously monitored. Control of the operating parameters and the collection of data is facilitated by the DAS.

The model utilized in this study is a Cahn TG-171 which has a maximum operating temperature of 1700°C. The balance has a sensitivity of 1 μg, a 100 gram weight maximum and a 10 gram dynamic weight range.[13] The balance sensitivity is affected by interferences such as static and vibrations.

Thermogravimetric analyzers are often used in similar studies of fossil fuels (such as coal and crude oils). For example, the TGA is useful to estimate kinetic and thermochemical data for reactions taking place during combustion; data such as activation energies, pre-exponential factors and rate constants.[14]

The TGA furnace consists of a circular, ceramic reactor tube surrounded by heating rods, as is shown in Figure 3.2. With this configuration, i.e. reaction gas blowing upwards in a circular reactor tube, there is only a certain part of the reactor tube that is at a uniform temperature. This area of the reactor tube is called the Uniform Temperature

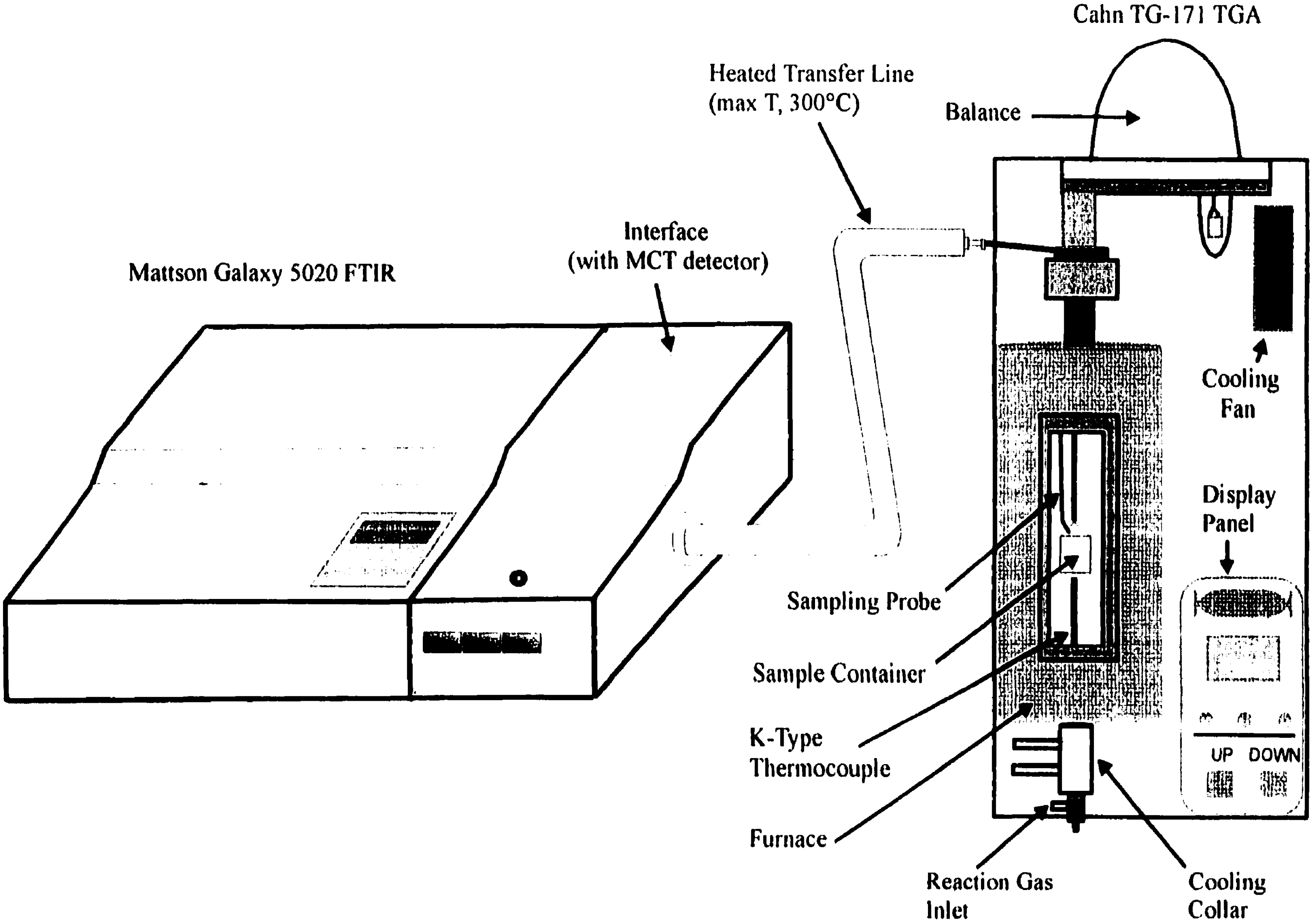


Figure 3.1: TG-FTIR Setup

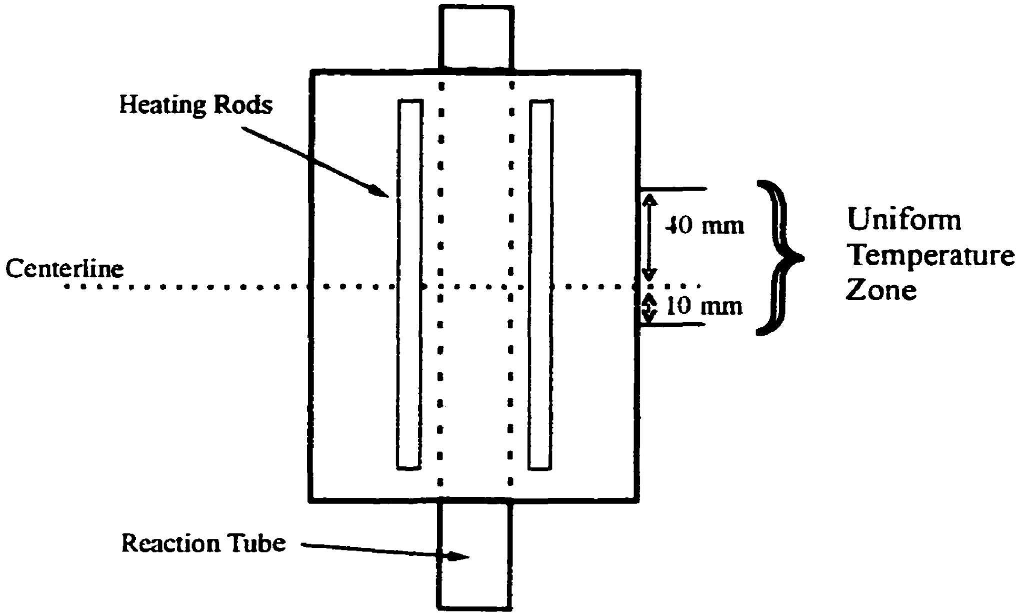


Figure 3.2: Interior of TGA Furnace

Zone, UTZ, as is shown in Figure 3.2. The sample to be analyzed and the temperature measuring device are to be placed within the UTZ for proper results to be obtained. The location of the UTZ depends on the flow conditions utilized but is generally about 50 mm long and slightly off-centered. Within the UTZ, a common assumption is that the sample temperature is the same as the furnace temperature.[14] However, when highly exothermic reactions are involved, as is the case for oils, the sample temperature will be higher than the furnace temperature.[14]

The oil sample being studied is placed within an alumina, cylindrical container with a 2 cm internal diameter. The container has a smooth surface to prevent the oil from soaking into it. The sample container is placed within the reaction chamber and is heated at a user specified rate to a temperature set by the user. Control of temperature and heating rate within the reactor is aided by the placement of a thermocouple approximately 1 cm below the sample container. Reaction gases enter from the bottom of the reactor tube and flows upwards and around the sample container, as is shown in Figure 3.1.

As the oil sample is subjected to the heating conditions specified, it undergoes physical and chemical changes. In this setup, some of the changes can be monitored directly. First of all, the sample container is suspended directly from a rod connected to an electronic balance. This allows for the recording of the oil weight as it undergoes the heating process and will give an overall measure of how fast the process is taking place as well as at what temperature range.

3.1.2 Gas Sampling Accessories:

In order to enhance the information the TGA provides, the experimental setup utilized several gas sampling accessories to monitor the emissions from the combustion-like process studied. The gas sampling accessories consisted of a sampling probe, a pump and a transfer line to take the sample to an external measuring device. The sampling probe location as well as the transfer line can be seen in Figure 3.1.

A more detailed schematic of the gas sampling accessories is shown in Figure 3.3, including a picture of the actual setup. The sample hangs from a sapphire hanging rod that is surrounded by a baffle system to direct flow of evolved gas away from the balance. The sampling probe, whose tip is located directly above the sample container to minimize dilution of the sample from the reaction gas, consists of a one piece 1/16" incanel tube that goes from the sample container to the connecting ring. The sampling tube fits snugly into a 1/8" incanel tube which is bent into the connecting ring, toward the transfer line. The connecting ring also includes a vent tube to allow the unsampled emissions to escape. The sample is drawn by a parastaltic pump at an approximate flow of 60 mL/min. The pump, which consists of a Masterflex 7543-30 pump drive (operating at 30 rpm) and a Masterflex L/S Quick Load pump head, operates at a pressure of approximately 0.85 atm. The transfer line which consists of an insulated 1/8" OD stainless steel glass-lined tube, is heated to a temperature of 250°C that minimizes the condensation of hot combustion gases produced. The transfer line, in this case takes the sampled gases to be analyzed to an FTIR. To further minimize condensation of the combustion gases, the connecting ring shown in Figure 3.3 is wrapped with an external heater and insulation which maintains this part of the accessory at 200°C.

3.1.3 Fourier Transform Infrared Spectrometer (FTIR):

The gases that are sampled from the Gas Sampling Accessories are analyzed with a Mattson Galaxy 5020 Fourier Transform Infrared Spectrometer (FTIR). The FTIR is

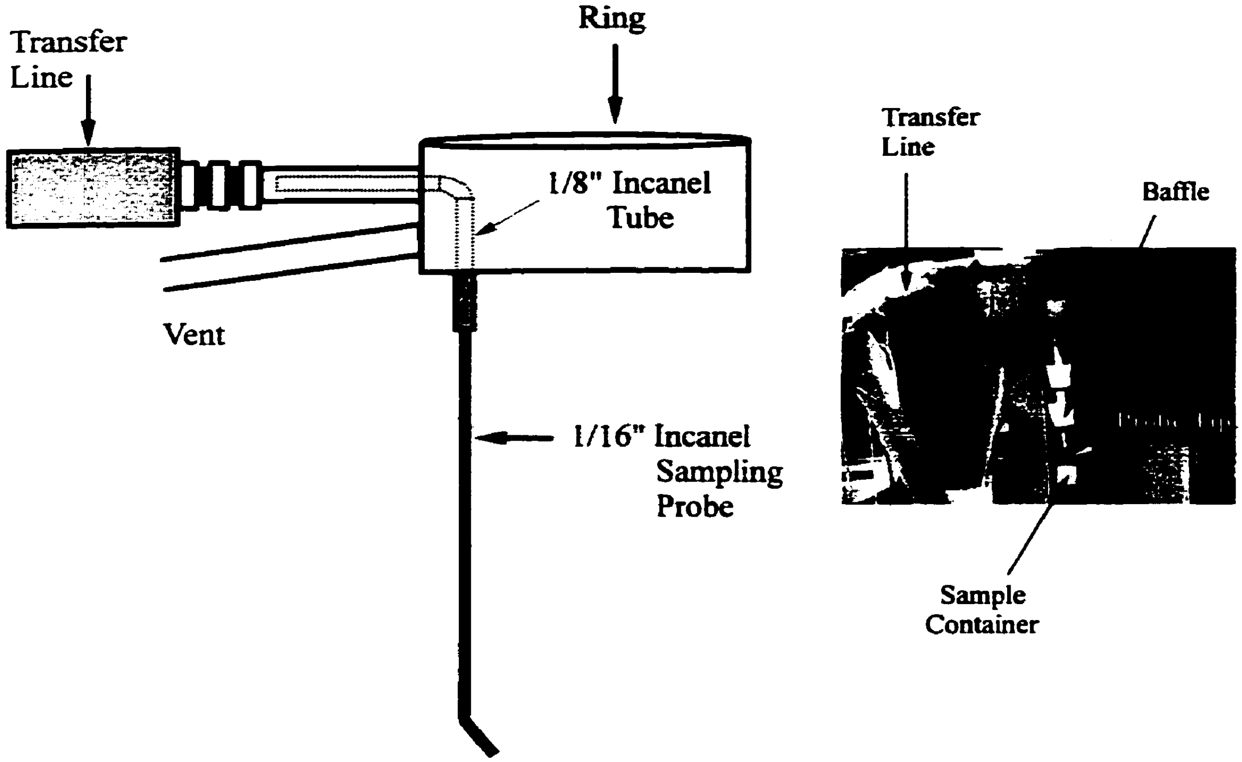


Figure 3.3: Gas Sampling Accessories

capable of determining the functional group composition of the gases analyzed. The FTIR produces a spectrum whose peaks can be associated to specific functional groups[15] (e.g. a C=C will manifest in a certain region of the FTIR spectrum). They have been used consistently as continuous emission monitors for volatile organic compounds emitted from a variety of processes, such as incinerators, since an FTIR is capable of analyzing multiple compounds simultaneously with high sensitivities.[16]

The FTIR used is equipped with a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector, a KBr beamsplitter and a 15 mL gas cell. Although spectra were generally collected at a resolution of 2 cm^{-1}, the model utilized is capable of resolution as fine as 0.75 cm^{-1} [17] which may be needed for gas-phase precision analysis. This model of FTIR consists of an external gas sampling compartment to allow for continuous monitoring of the sample taken by the Gas Sampling Accessories. An image and a schematic of this external gas sampling interface is shown in Figure 3.4. The gas to be analyzed enters the interface from the transfer line, as is indicated on the diagram. The

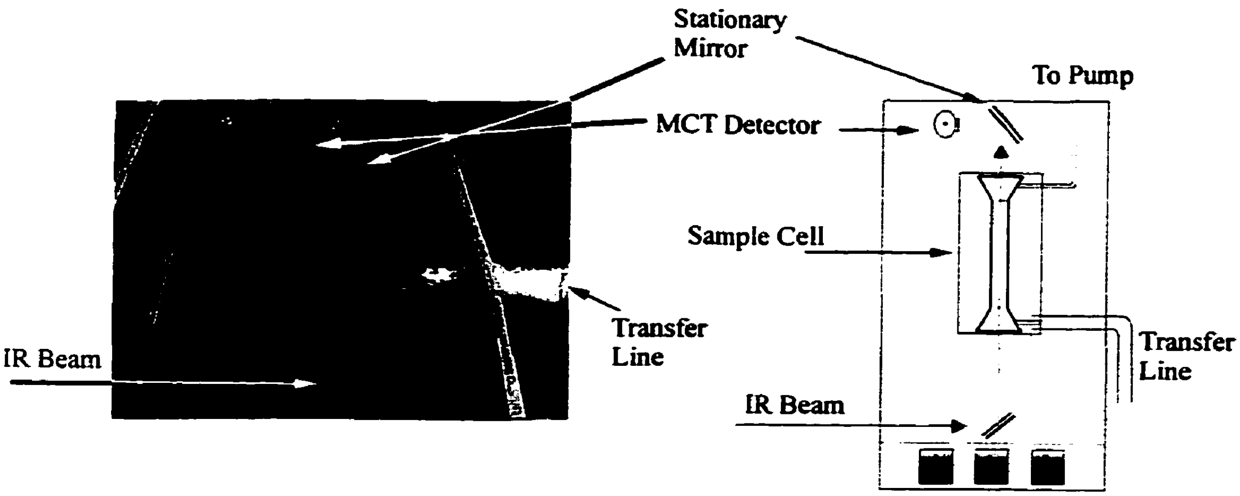


Figure 3.4: FTIR External Gas Sampling Interface

sample enters the Sample Cell, where the IR beam is passed via two stationary mirrors. The pump that draws the sample is located after the Interface. Finally, the MCT detector utilized by the FTIR is also included in this compartment.

3.1.4 <u>TGA-FTIR</u>:

The FTIR is used in conjunction with the TGA in order to analyze the gas-phase release resulting from the programmed heating profile. In addition to observing the material weight changes with respect to temperature and time, the placement of a sampling probe located at the top of the sample container allows a portion of the gases generated during the process to be sampled. These gases then travel through a heated transfer line and continuously pass through an FTIR gas cell. This allows for fairly continuous observation of the changes in the chemical composition of the released gases and by extension, gives insight into the changes taking place in the oil sample in the furnace. In addition, changes in the sample weight and temperature inside the furnace are measured continuously, which allow for understanding of the processes taking place.

3.2 Analytical Instruments

A number of different analytical instruments were utilized during the research to study different aspects of the process, after the thermal remediation process was complete.

3.2.1 Scanning Electron Microscope (SEM):

A Scanning Electron Microscope (SEM) was used to study the solid particle morphological evolution. The model used was a Jeol 840. Images were collected with a beam current of about 240 mA and an accelerating voltage of 20 keV. The SEM allowed for viewing the surface of the particles generated during the heating process, up to a magnification of 700 times. By observing the particle surface and how its characteristics change with temperature, it is hoped that an understanding of the processes the particles undergo can be achieved.

3.2.2 Energy Dispersive X-Ray Spectrometer (EDS):

Qualitative analysis of metals found on the surface of the solid particles generated during the heating process was also attempted. The instrument utilized for this part of the study was a Tracor Northern 820 Energy Dispersive X-Ray Spectrometer (EDS) operated at a 10 keV beam.

3.2.3 Optical Microscope:

The solid particles generated during the process were also viewed under limited magnification using an optical microscope. The model used was a Neophot 21 Optical Microscope and it allowed for magnifications of 25 and 40 times.

3.2.4 High Performance Liquid Chromatograph (HPLC):

Analysis of vapor phase Polycyclic Aromatic Hydrocarbons, after extraction from an organic vapor trap, was performed using a Perkin-Elmer LC250 High Performance Liquid Chromatograph with a LS-40 fluorescence detector. The system utilized had a detection limit of approximately 0.001 μg/mL.

Chapter 4: Method Development & Methodology

4.1 Introduction

As described in Chapter 2, the purpose of the research is to study the behavior of waste oil in a combustion-like process. The process needs to be slow enough so that the physical and chemical changes that the oil undergoes can be observed. In a typical burning process, the kinetics of the process are too fast to allow for observation. Therefore, the set of conditions that need to be applied to the waste oil study need to be such that the kinetics of the combustion process are lowered. The major factor affecting kinetics (i.e., reaction rates) is temperature; the higher the temperature, generally, the faster are the reactions that take place. Therefore, it was deemed imperative to have a very good control over sample temperature for the study. At the same time as being able to control the temperature by ramping it slowly, a low final temperature would also be required.

Therefore, it was decided to study the process by slowly heating the oil so that factors other than kinetics would determine process rates. Process rates will be determined by the rate of the temperature ramp rather than by the reaction kinetics which will allow for processes such as vaporization to be observable. Another aspect of the process that would be more visible is the reaction of the oil components with oxygen. Since diffusion is a slow process compared to kinetics, slowing down the kinetics of the process should make the diffusion process more observable.

The desired conditions were therefore achieved by simulating the combustion process using a Thermogravimetric Furnace (TGA) coupled with a Fourier Transform Infrared Spectrometer (FTIR) for on-line gas phase analysis of the products emitted from the process. The TGA system, with the aid of computer control, allows for the heating of the sample at a rate desired and allows for the flexibility required in order to facilitate future parametric studies. This combination of instruments also allows for the continuous monitoring of both sample weight and gaseous evolution as a function of both time and furnace temperature which will have the desired effect of observing the process closely.

The first objective is method development, i.e. determine what conditions to apply to the sample in order to be able to do what was set out to be done. This was accomplished by altering conditions of the TGA-FTIR system in order to establish feasible operating parameters. Operating parameters such as furnace heating profile as well as FTIR settings to be used were determined in this part of the work. At the same time as setting these parameters, it is possible to gain some insight into sample behavior so that a baseline can be established to use as a reference point against future work.

4.2 Preliminary Experiments

In order to establish the conditions at which the future study would be carried out, it was necessary to do some preliminary investigations into the behavior of both the material being studied and the characteristics of the TGA-FTIR system. Both of these would need to be considered when deciding upon the conditions and included the following:

- heating rate
- sample amount
- reaction air flow rate used
- FTIR settings (e.g, resolution, # of scans, spectral frequency)

Approximately 20 various preliminary experiments were done in order to establish these conditions for study. For these preliminary experiments, Oil 1 was utilized only. The conditions selected needed to be sufficient to allow for the set objectives to be achieved; i.e., allow observation and interpretation of events occurring during the process on a general level. Once this fundamental understanding is achieved, optimization of the instrument conditions could be attempted.

4.2.1 Initial Attempts:

The first trials undertaken had the goal of familiarization with the instrument and the material. The maximum heating rate allowed by the instrument for low temperature applications is 100°C/min. Although the project goal is to slow down the combustion process, it was not clear as to the degree of slow-down required to allow for distinguishing events. Therefore, the first attempt made was at the maximum heating rate possible, i.e. 100°C/min, which is still slower than an actual combustion heating rate. Also, it was not clear as to how much sample to subject to the heating process. In order to get sufficient residue for solid studies after the process is over, one gram of oil was utilized for first attempts. Air flow during the run was arbitrarily selected at 53 mL/min (which was suggested as a typical flow rate by the instrument manufacturers and was similar to that used for crude oil/solid mixtures[14]).

The result of applying these conditions to Oil 1 was a one weight loss region in which the rate of weight loss was much too severe (the approximate rate of weight loss was calculated as 500 mg/min). This caused the balance to read a large negative value during this time period (> 1.5 g) since the process released a large and sustained amount of vapors that forced the balance arm upwards. The emitted vapors provide a sufficient upward force that supports the hang-down assembly, thus causing an apparent weight loss in the balance data collected. The sample lost its entire weight in about two minutes at a temperature of approximately 500°C and no ash remained in the container at the end of the process (probably entrained with the vapor release). It was clear that these conditions were unacceptable for the required purposes and would have to be slowed down further.

After this attempt at these conditions, the heating rate was lowered to 10°C/min since it was clear that the process needed to be slowed down to hope to avoid the previously seen negative weight reading. Also, since no residue was found previously, it was decided to utilize a larger initial sample, namely 1.6 grams and the air flow rate was kept the same. Under these conditions, the negative weight reading previously observed was avoided and the weight loss behaved smoothly. The weight loss now occurred over a 27 minute period at an average rate of weight loss of approximately 56 mg/min. This process occurred between 250°C and 400°C (and therefore at a lower temperature than at the previous conditions, i.e., 100°C/min and 1 gram). This time, residue did remain in the container in a sufficient quantity for study (5 mg).

Unfortunately, after these runs, a significant amount (~10 mL) of a light brown condensed material was found collected on the bottom of the furnace reactor tube. Therefore, before investigating the process further, it was necessary to determine the source of this material in order to prevent it in the future. The possible collection of this material in sensitive areas of the instrument could do serious damage, especially to the sensitive balance system. Also, at higher temperatures, it is likely that this material will react, thus potentially affecting the integrity of the FTIR results.

4.2.2 Visual Observations:

The condensing material source could not be identified during TGA runs and could only be confirmed through visual observation of the process. Since the inside of the reactor chamber is not accessible during the heating process, the sample container was placed in a conventional oven with viewing access possible. Although the heating rate was comparable (i.e., ~ 10°C/min) and the final temperature was 600°C, the environmental conditions in this setup were quite different than for the TGA setup. There were openings in the furnace to allow air to enter, but there were no controls on the amount of air entering. Also, whenever the door was opened to make observations on the process, large amounts of air were introduced into the system.

Despite these differences in environmental conditions, typical characteristics of the process could be observed and hopefully, an explanation for the condensed material would be achieved. (It was feared that the oil within the container was bubbling or spilling over the sides to fall down into the bottom of the reaction chamber.)

Under these conditions, three runs were completed and the following observations were made. In general, the observation was made that the burning process occurred in two distinct temperature regions. A flame was observed at approximately 200°C, with the sample still in a liquid state. The flame extinguished while the sample was still liquid and another flame appeared when the material looked like a tar phase. This occurred approximately at 350°C, with some of the material being propelled from the container due to "sputtering". (This material was black and tar-like and did not seem anything like the condensed material found in the TGA furnace.)

Upon further investigation, it was found that in the ASTM Standard Method for Ash Determination (i.e., ASTM D-482), the same sputtering effect is avoided by first burning the oil at low temperatures, to remove all volatiles prior to subjecting the remaining "tar" to a high temperature oven[18]. In this way, no volatile matter will be left to sputter out of the solid residue, which would take some residue with it and would corrupt the ash determination experiment. This probably explains why, for 100°C/min attempt, no solid material remained in the container and why for the 10°C/min attempt, less residue than expected remained.

Although these observations would prove to be interesting in comparison to the future study, the most significant observation made was that at about 175°C, a brown liquid film was seen coating the upper inside walls of the container. This film had the same visual characteristics as the condensate found in the reactor. This led to the conclusion that, at low temperatures, a fume is probably released that easily condenses on surfaces. This material finds its way to the bottom of the reactor while the uniform temperature zone is still relatively low. Since other sections of the TGA system are not temperature controlled, they are cooler and thus the fumes condense and collect at the bottom of the reactor. The observations proved that this condensation did not result during the major weight loss period of the heating process and was therefore not due to sputtering.

It was therefore concluded that, since the heating rate utilized needs to be slow (for reasons previously discussed), it would not be possible to eliminate the formation of these fumes. Therefore, to avoid instrument contamination, it was necessary to minimize the deposition of this material (and periodically clean the instrument). The only alternative to do this was to drastically reduce the amount of initial material used in the study at the expense of getting less final residue to study.

4.2.3 Lower Mass & Increased Air Flow:

The result of the visual observation was that in order to attempt to minimize condensation, less initial sample should be used. Therefore, the sample weight was reduced to roughly 320 mg for the next set of experiments. The flow rate of air was also increased from 53 sccm to 79 sccm to help push some of the fumes up and out of the venting system. To counteract the increased air flow which would probably increase combustion reactions (i.e. more oxygen available for oxidation), the process was further slowed to a 5°C/min heating rate. Under these conditions, the heating time was about 3.5 hours while cooling was about 4 hours.

Three runs were performed with weights of 318, 317 and 323 mg. The weight loss curves began to clearly demonstrate two different regions, separated by an inflection point. This behavior in the weight loss is consistent with what was seen in the visual observation experiments (namely, a separate lower and higher temperature reaction zone).

Surprisingly, despite lowering the heating rate, the second part of the weight loss curve again showed severe negative readings for two of the three runs, as was seen with the 100°C/min run. (The third run did not exhibit a negative reading but was very unstable.)

When comparing these conditions to the previous (which did not give negative readings), a much smaller sample size was used (i.e., 320 mg as compared to 1.6 g), a slower heating rate was used (i.e., 5°C/min versus 10°C/min) and an increase in air flow was utilized. Therefore, either sample amount or air flow or both affect the weight loss behavior towards a negative value. The lowering of the heating rate would clearly slow down the process, whereas the affects of the other two are unclear. Since, after the visual experiment, it was decided that it was more important to keep sample size low and increase air flow rate, the process conditions were still not acceptable for purposes of the study and thus lowering the heating rate further was the only option remaining to have a smooth non-negative weight loss behavior.

4.2.4 Inert Medium (Pyrolysis):

Prior to attempting to further slow down the heating rate, it was thought that perhaps studying the process under pyrolytic conditions would be a better option to avoid rapid oxidation. Therefore, the same conditions applied above were utilized but with nitrogen replacing air, in order to see how the different processes compared. If pyrolysis runs proved to alleviate the weight loss curve difficulties and the condensation problems experienced using an oxidative environment, it may be possible to study the system under pyrolytic conditions instead of oxidative ones.

Therefore, a nitrogen flow was used to replace the previously used air at a comparable rate (i.e., 81 mL/min). The heating rate was kept the same, at 5°C/min. Two runs were performed with weights of 313 mg and 321 mg, again comparable to the previous weights used. In both runs, a stable and non-negative weight loss curve was obtained, but with only one distinct region showing.

However, despite this obvious advantage over the oxidation experiments, the pyrolysis runs resulted in parts of the instrument being covered with a black, charcoal-like material embedded in the ceramic material. Although this material was removed by baking the furnace under oxidative conditions, it was feared that damage could be done in the long term. Also, the FTIR spectra taken showed an as yet unexplainable lag with respect to the weight loss (i.e., the peaks obtained appeared later than expected based on the weight loss curves). Therefore, although pyrolysis showed improvement in weight behavior characteristics, the contamination was judged to be too severe to proceed with further pyrolysis studies.

4.2.5 Reduced Heating Rate:

Therefore, it was decided to continue the study using an oxidative environment since it would be more representative of actual combustion systems. This meant that the heating rate needed to be slowed down further to get a more stable weight loss curve and that the limitations of weight size and condensation would have to be accepted. These limitations would remain at least until such time that the process was better understood and that the effects of each parameter on the weight loss could be determined.

The heating rate was lowered to 3°C/min and the sample size kept the same. It was hoped that doing so would not only eliminate the negative weight readings (i.e. stabilize the weight curve) but it would allow the two regions of the curve (that was previously only slightly seen) to be seen much more clearly and an attempt to better characterize these two regions could be possible. This heating rate proved to do both stabilize weight readings and distinguish clearly between the two weight loss regions. In a similar TG experiment on mixtures of heavy oil and solids, heating rates between 2°C/min and 20°C/min were utilized.[14,19] In another study, much lower heating rates of 0.25-0.83°C/min were used.[9] Therefore, the heating rate determined here would seem to be logical since a lubricating oil is used in this study. Therefore, it was decided to continue all other studies using this heating rate. Although the heating rate could be lowered further, doing so would result in an increased run time and data file. The increase could not be justified yet, until more was known about the process behavior.

4.3 Experimental Conditions

After many preliminary experiments, a set of conditions was found that was used thereafter for all studies. A summary of the experimental conditions used, including heating profile, is shown in Figure 4.1. About 300 mg of the waste oil being studied is heated from an initial temperature of 30°C to a final temperature of 1000°C. An initial heating rate of 3°C/min is applied from 30°C to a temperature of 650°C, which allows for the process to be slow enough for observation. An air flow of 79 mL/min is used for all subsequent experiments (i.e. oxidative environment). The process is stopped at a final temperature of 1000°C since in most practical cases, waste oils are not generally burned above this temperature. By 650°C, both the evolution of gas-phase products and the weight loss were determined to be complete since all data curves were generally flat after this point. After 650°C, it was assumed, based on these observations (and subsequently proven) that the oil sample was in the solid form. Because of this and the assumption that the heating rate had less effect on the morphological changes of the solid residue (since the processes involved are much slower), the experiments are expedited by slightly increasing the heating rate to 5°C/min from 650°C to 1000°C. The sample is kept at 1000°C for 60 minutes. (This is necessary in order to clean the furnace of some organic condensation that takes place earlier in the heating process, as was previously discussed.) The entire heating process takes 5.5 hours, after which the remaining material is allowed to cool slowly. In all cases, a natural cooling of the furnace with shop air was applied.

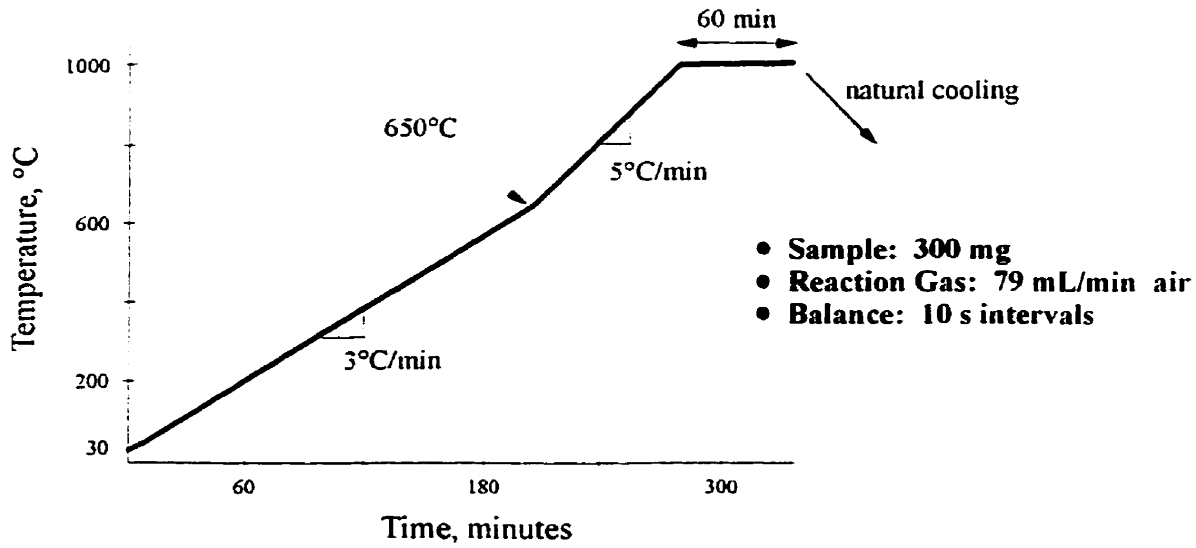
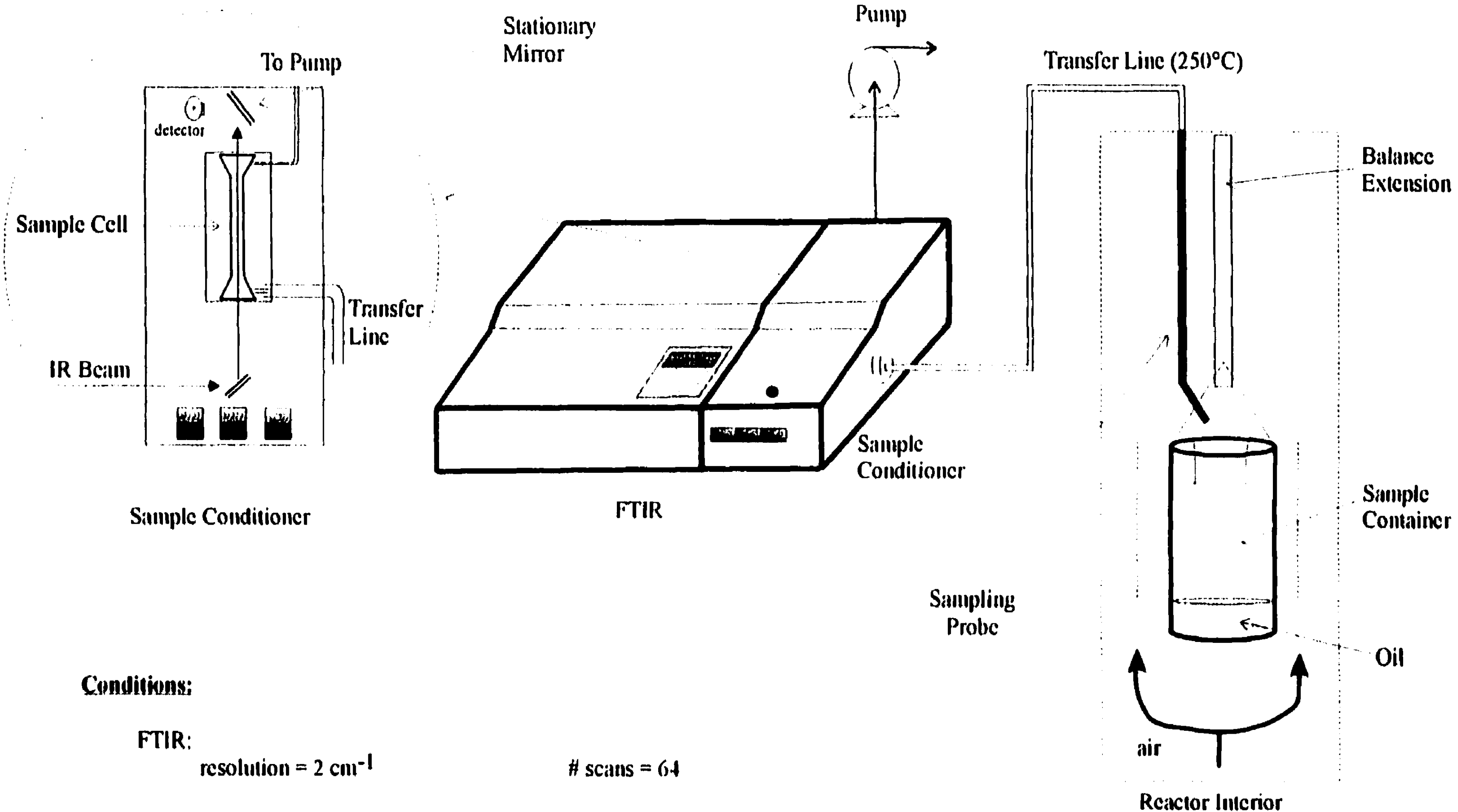


Figure 4.1: Furnace Conditions

The selection of the sample amount, i.e. 300 mg, was made so as to have enough material to maximize the ability to detect any emissions that would otherwise be released in too small a quantity. On the other hand, too much material would risk saturating the FTIR's ability to detect trace amounts of some compounds and thus, too much sample could not be used either. The amount of 300 mg of waste oil was found to be an acceptable compromise, especially with respect to condensation, as previously described (i.e., want to maximize emissions but avoid saturation and minimize condensation). (Note that due to the setup and the volatile nature of the sample, it was not possible to gain an accurate initial weight reading. In order to do so, it would have been necessary to wait for a long time for the balance to stabilize and it was feared that this would allow a portion of the sample to volatilize while waiting. As it turned out, at such low temperatures, an insignificant amount of sample is lost. Therefore, in the future, if more accurate weight readings are required, balance stability can be attained prior to beginning the run without the risk of losing material.)

Due to a combination of small sample weight used in the study and the low temperature applied, the attempts made at capturing soot (solid particles in the gas phase) proved to be in vain. There was insufficient material generated for any study and since more sample could not be used until the condensation difficulties were alleviated, the study of soot was left for a future time. Soot release is an area of concern since PAHs are associated with the formation of this material and PAHs are considered hazardous.[20]

Gas-phase data collection was affected by FTIR settings. Spectra were collected at a resolution of 2 cm^{-1} by co-adding 64 scans, generating a spectrum every 18 seconds. Samples were drawn continuously by parastaltic pump at a flow of approximately 60 mL/min through a gas-phase sampler (see Figure 4.2). The FTIR conditions (i.e. resolution and number of scans) were manipulated so that sampling frequency could be similar to gas residence time in the sample cell. By ensuring this, it would be unlikely that some compounds escape detection prior to a spectrum being taken. (Also, since the heating process is slow, this would be even less likely to occur since changes in the process should be gradual.) The cell volume is 15 mL and with a sampling flow of 60 mL/min, the gas residence time is 15 seconds. Therefore, the spectra generation frequency, i.e. one every 18 seconds, is comparable to cell residence time and will allow, with reasonable assurance, that very little information would be lost through gas



Conditions:

FTIR:

resolution = 2 cm^{-1}

scans = 64

scan time = 18 seconds/spectrum

cell volume = 15 mL

Pump flow rate = ~60 mL/min

Figure 4.2: Gas-Phase Sampling Conditions

constituents circumventing the sampling process. Finally, in order to minimize dilution of the drawn sample by the reaction gas, the sampling probe is placed directly over the sample container (see Figure 4.2).

4.4 Data Interpretation

Figure 4.3 shows a typical TGA-FTIR data curve obtained from the data acquisition software called TEA, Time Evolved Analysis. The information shown in the figure represents the data collected for one data point. On the upper part of Figure 4.3, there are two curves: a Total Infrared curve (IR) and a Weight Percent curve (Weight), both plotted versus run time. The lower curve gives the sample weight behavior obtained from the TGA balance data. The particular run shown in Figure 4.3 lasted about 3 hours. The weight curve gives indication of the physical changes that the sample undergoes during treatment. The upper curve represents a total infrared chromatogram and results from data collected by the FTIR, via the gas sampling accessories. The total infrared curve is a summation of the individual spectra which are taken at constant intervals (i.e. every 18 seconds) throughout the entire heating process. An example of one such spectrum is shown at the bottom of the figure and is plotted as Absorbance units versus wavenumbers, in cm^{-1}. This spectrum was taken after 72.68 minutes of run time and corresponds to the point in the heating process where the temperature was 240°C, as is noted in the upper curve in the form of a vertical line. (All pertinent information concerning this spectrum, i.e. run name, run time, temperature, and weight information, is shown in the form of a caption on the top of the spectrum curve.) From this curve, it is possible to attempt to determine the functional group composition of the gases that are sampled at that exact point in the heating process.

How the compositional determination of the sample gas can be achieved is explained by looking more closely at a similar spectrum as the one shown in Figure 4.3. This is shown in Figure 4.4 where the plot consists, again, of the standard absorbance versus wavenumber configuration for FTIR spectrum plots. The peak identification can be accomplished by comparing the obtained spectrum in terms of peak location, peak shape and pattern to standard spectra taken of the material in a pure form.[21] A spectral

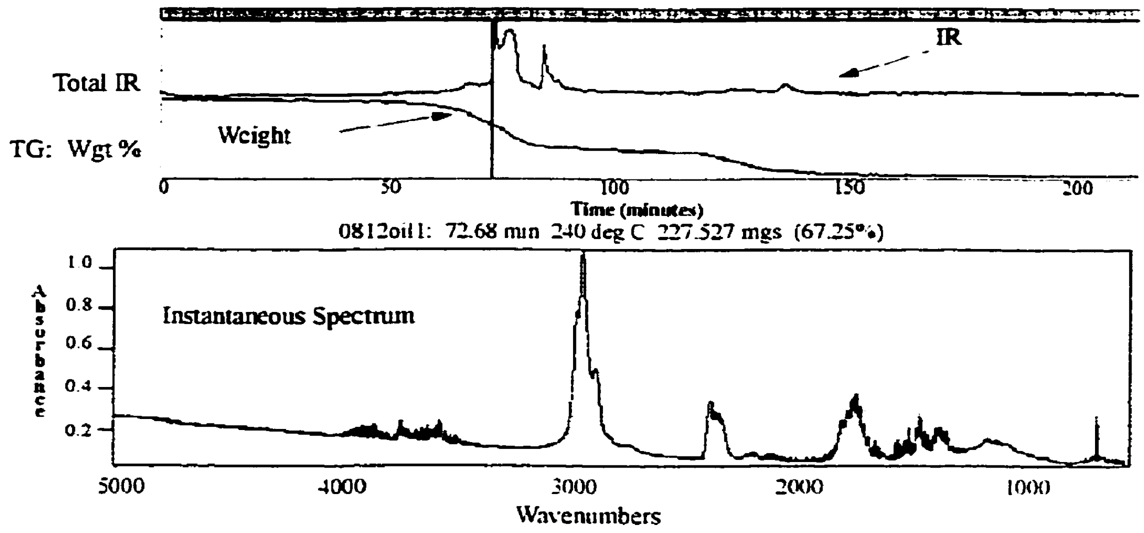


Figure 4.3: Typical TGA-FTIR Data Curves

feature can be identified when the signal to noise ratio is greater than four.[16] (Some of these standard spectra are shown in Figure 4.5 and were taken from the NIST/EPA Gas Phase Infrared Database.) Once identified, a representative peak location is used to represent the compound in future studies.

The major compounds that can be identified in the spectrum in Figure 4.4 are CO_2 (2300-2380 cm^{-1}), CO (2050-2200 cm^{-1}) and water (1780-1900 cm^{-1}).[21] There are other compounds that could be identified in theory with the FTIR and may be emitted during the heating process. Although the samples studied contained insignificant amounts of nitrogen, samples with nitrogen could generate products such as ammonia, nitrous oxide and nitrogen dioxide. None of these compounds were detected during the study. These compounds have identifying peaks at 950 cm^{-1} (ammonia), 2200 cm^{-1} & 1300 cm^{-1} (nitrous oxide) and 1900 cm^{-1} (nitrogen dioxide).[21] As can be seen in Figure 4.4, these peaks were not visible (even after subtracting the interfering peaks of CO_2 and CO). Also, there is over 1 wt% of chlorine in Oil 1. Chlorine, during combustion, generally forms HCl which manifests itself as a peak at 2670-2850 cm^{-1} on the FTIR spectrum.[21] Since this peak overlaps with the much stronger hydrocarbon peak, no HCl could be identified for Oil 1, although some is expected. (It was not possible to subtract the hydrocarbon peak from the spectrum since the exact compound could not be identified.)

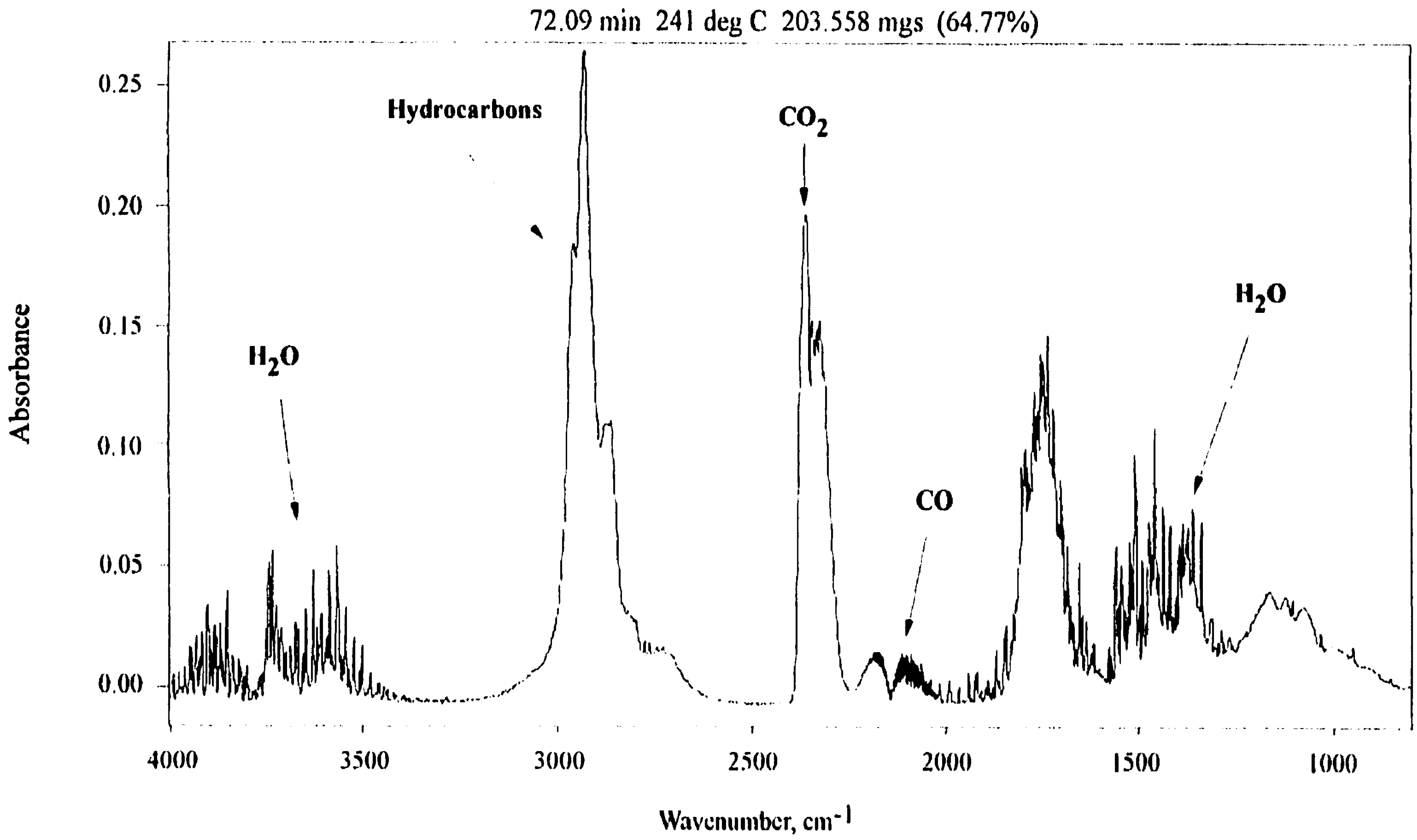


Figure 4.4: Typical Infrared Spectrum

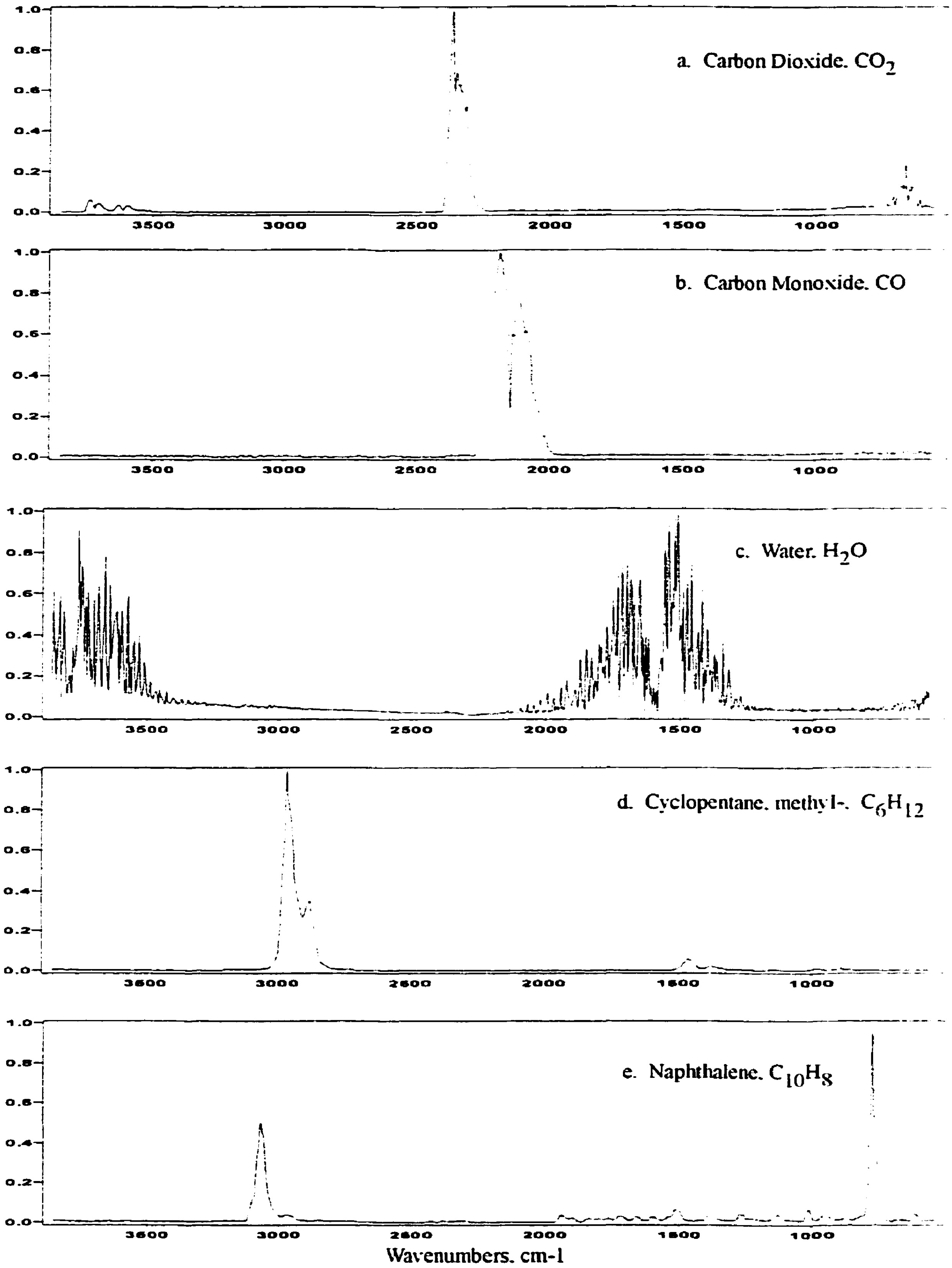


Figure 4.5: NIST-EPA Vapor Phase Infrared Library Spectra

It can be seen in Figure 4.4 that, at this particular point in the run, there are peaks representative of CO_2, CO and H_2O which can be clearly identified when compared to pure vapor phase spectra of the same compounds found in Figure 4.5a,b& c, respectively. There is also a peak representing some hydrocarbons at 2700-3000 cm^{-1} region (peaks in the 2875-2975 cm^{-1} range having 3 sharp peaks represent aliphatic C-H stretching vibrations [22]). The peaks in this region cannot be assigned to specific hydrocarbons since it is most likely that different types of hydrocarbons are found at the same time and whose peaks are found in the same general location.[21] (An example of a hydrocarbon spectrum is shown in Figure 4.5d.) There is also an unidentified peak consistent with a carbonyl functional group, C=O, which usually shows at 1700 cm^{-1}.[22] This peak was consistent throughout all runs but cannot be identified as yet. In terms of aromatic compounds, these would manifest themselves as peaks in the 3050 cm^{-1} region[22] (i.e. to the immediate left of aliphatic hydrocarbons) and therefore, none are detected in this spectrum. (An example of an aromatic compound spectrum is shown in Figure 4.5e, for naphthalene.)

Figure 4.4 also shows how nicely the compositional information that the FTIR can provide is linked to the TGA information through the caption at the top of the curve. Not only is an indication of the gas-phase composition obtained, it is correlated to the exact time and temperature the sample was taken at, as well as the sample weight and % weight remaining at the time of the sampling. Therefore, this one figure gives a good overall informative picture of how the two instruments complement each other and allow for partial interpretation of what is occurring to the oil during the heating process.

The data collected in the above-mentioned format was used to generate evolution profiles for both weight and gas-phase components. The curves generated for the gas phase is a method known as Evolved Gas Analysis. This was done to transform the data into a format more conducive to following the process behavior and therefore, facilitate interpretation. The evolution profile format is very valuable when a mixture of products is generated since it will give clues as to the chemistry of the reactions occurring. What may appear as a single weight loss on a TGA curve could be seen as more through the evolution profile observations. Therefore, the profile approach may make it possible to detect subtleties in the reaction process being monitored.[21]

The data is collected very frequently from both the TGA balance and the FTIR (namely, once every 10 seconds for the weight and every 18 seconds for spectra). Despite this frequency, during the preliminary study, it was clear that the slow heating caused changes in the process to be gradual enough so that such frequency was not necessary for generating smooth evolution plots for the entire temperature domain. In certain areas of the process, events occur more rapidly and thus it may be necessary in the future to study these areas more closely. Since, once set, the sampling frequencies cannot be changed during a run, it was decided to collect more data than immediately necessary in the event that a closer look at the evolution profiles was warranted. Therefore, evolution profiles generated from the TGA-FTIR data were done so at 5°C intervals (which is equivalent to a data point every 100 seconds in terms of weight data). This proved to provide sufficient data points to study the process at least at a level discussed in the thesis. If, however, in the future, it is found that more detailed information is required, finer data points can be utilized to generate the profiles. Also, if so required, sampling conditions for the FTIR (and the balance) can be altered to make sampling more frequent and refine the evolution plots generated. (Note that, in so doing, other aspects such as spectral quality and computer file size, are negatively affected and thus, alterations would need to be justified.)

An example of an evolution plot generated in this way is shown in Figure 4.6. This figure shows the evolution of CO_2 gas as well as the sample weight behavior so that the two can be easily related. This was generated from using the data in the form shown in Figure 4.3 at every 5°C interval. The TG-FTIR format gives temperature and weight data which are used directly to generate the weight curve in terms of weight percent (i.e. current weight divided by initial weight times 100). However, for the CO_2 profile, the height of the peak corresponding to CO_2 was plotted by taking the difference between the absolute peak absorbance and the baseline absorbance, giving a net absorbance. Generated this way, the curves were smooth and no apparent loss of information caused by skipped data points seemed to occur.

The evolution generation procedure must be kept in mind when interpreting the curves in later sections. Since the plots were generated in 5°C intervals, any association of temperature to events can be no more accurate than within 5°C. If a finer accuracy is

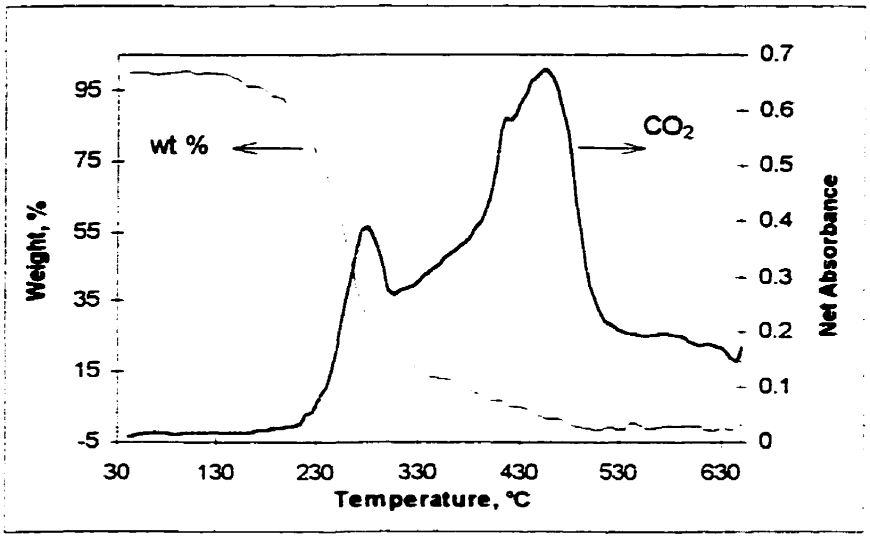


Figure 4.6: Example Of A Gas Evolution Profile

deemed necessary, the plots can be regenerated from existing data using a finer data frequency. The frequency limitation, at least under the current conditions would depend on the balance data collection frequency (every 10 seconds) for the weight loss curve and the FTIR spectra collection frequency (every 18 seconds) for the gas evolution profiles. In terms of temperature, these limitations work out to 0.5°C (3°C/min*1min/60sec*10sec) based on the balance frequency and 0.9°C based on spectra. However, the data collected for temperature are recorded to whole numbers only. Therefore, in theory, the frequency of data collection in terms of temperature is limited to 1°C. In practical cases, however, since the heating rate is slow, and errors due to round-off occur, several consecutive data points may have the same temperature reading. When generating the profiles versus temperature, a decision thus needed to be made as to which data point to choose. In the curves shown, for consistency purposes, the first data point of consecutive, equal temperature readings were taken. However, since the heating rate is slow, the differences in data were not significant and thus, the overall curve would not be severely affected if either point was taken. A more finer evolution profile could be attained with the existing data if the data (e.g. weight percent and FTIR net absorbance) are plotted versus time instead. (Since the initial temperature of the runs varied slightly, profiles generated on the basis of run times would have to be shifted for the purposes of comparison.)

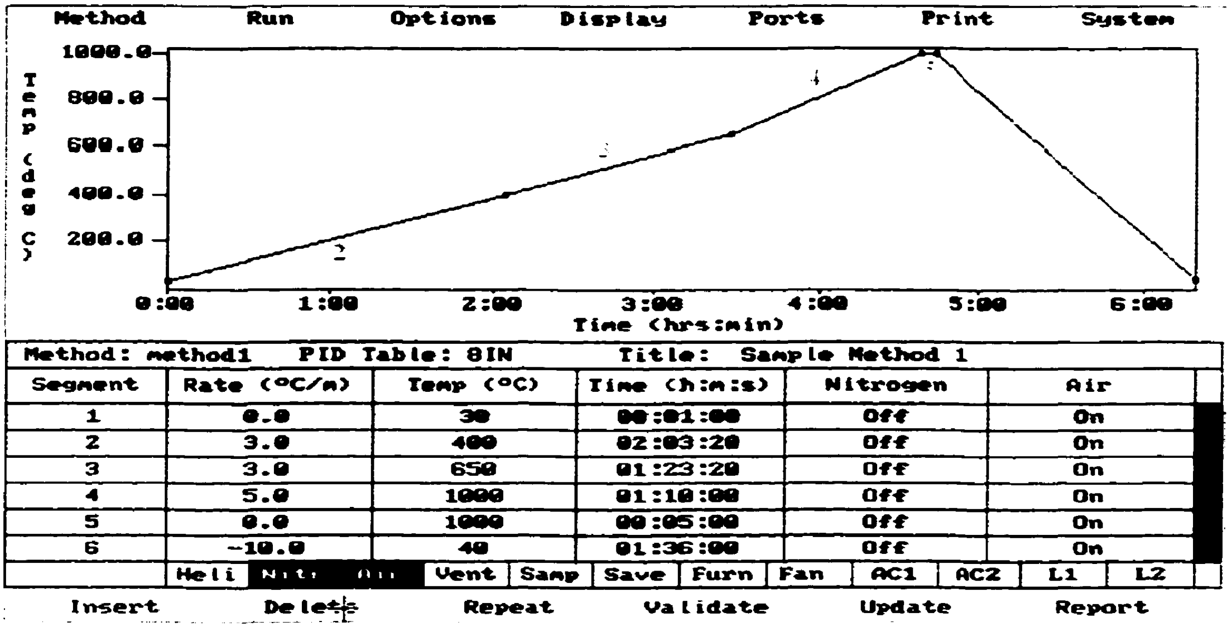
Finally, when the programmed temperature profile was compared to the actual temperature readings versus time, differences occur due to various considerations such as controller response and thermocouple accuracy. Typically, there was a 5 minute delay during the initial startup before the furnace temperature caught up to the programmed temperature. That is, it was not until a temperature of 45°C that the furnace and programmed temperatures were the same. Since very little weight loss occurred in this low temperature region, this lag is not considered detrimental to the study. However, for more rapid heating rates, it may become significant and affect observations made.

After this initial lag, the temperature differences between the two were excellent at low temperatures (differing only by at most 0.5°C, at temperatures less than approximately 100°C). At higher temperatures, the difference became gradually larger but was still acceptable. At 650°C, the difference was at its most significant, compared to lower temperatures, and was only at 8°C. This decrease in temperature accuracy is most likely a characteristic of the K-type thermocouple used, which is a low temperature device.

4.5 Repeatability

By using the TGA and its data acquisition software (DAS) to simulate the sample heating profile and conditions, it was possible to perform the study in a controlled and repeatable environment. An example of the programmed profile format of the DAS is shown in Figure 4.7. The software allows the user to set conditions in the form of segments for such parameters as heating rate (in °C/min), final temperature of the segment and time for segment completion. The resulting heating profile is also shown on the screen for easy reference.

Although the software does not allow for control of the various gas rates needed (which is accomplished via regulators and flowmeters), the DAS allows the user to engage or disengage the various gases. For example, as seen in Figure 4.7, the run is using air as a reaction gas. However, if the user so chose, the gas could be switched between the two gases at each segment so that a run could be performed using both gases at different points in the run. As far as the heating rates are concerned, the limit to heating rates utilized is due to the instrument and not due to the software. (For the temperature range



Method: method1 PID Table: 8IN Title: Sample Method 1

Segment	Rate (°C/m)	Temp (°C)	Time (h:m:s)	Nitrogen	Air
1	0.0	30	00:01:00	Off	On
2	3.0	400	02:03:20	Off	On
3	3.0	650	01:23:20	Off	On
4	5.0	1000	01:10:00	Off	On
5	0.0	1000	00:05:00	Off	On
6	-10.0	40	01:36:00	Off	On

Figure 4.7: Data Acquisition System Format

utilized, the maximum heating rate of the instrument is 100°C/min and the smallest attempted was 1°C/min having excellent response. However, the software allows smaller heating rates but the response is unknown.) Also, in terms of cooling rates, there is less control on them since no external cooling system is in place which limits how fast cooling can occur to that which occurs naturally.

Other parameters in the system can also be precisely controlled in the same manner to ensure repeatability between runs. These include "Data Save Mode" which specifies the type of data collected to be stored in a computer file (e.g., balance data only or balance data and FTIR data could be specified at different points in the run). Through the use of the DAS, the conditions to be applied can be set and stored for future use so that consecutive runs will have the same settings and thus, improve repeatability. The flows of gases still need to be visually verified as the DAS does not control gas flow.

4.5.1 Weight Behavior:

In order to get an appreciation of the repeatability of the experiments in terms of weight behavior, the weight profiles were plotted for five different runs that were believed to be under the same conditions (i.e., were run consecutively to avoid changes in operating parameters not controlled by the DAS such as thermocouple placement). The results are shown in Figure 4.8 using Oil 2 for demonstration. The reproducibility achieved was acceptably good. The profiles all had the same general shape but demonstrated some scatter. At the maximum difference, which occurred at approximately 260°C, the error obtained was ± 7 wt% (Position 2). However, the error was larger in this region due to the pronounced slope in the weight curve. The error in other regions of the curve was much less and could be typified by the error obtained at Position 1 on the Figure, at a temperature of about 50°C. The error here was ± 1 wt%. The overall error for the weight experiments ranged from 1 wt% to 7 wt%. Therefore, reproducibility and repeatability in terms of weight profiles was very good. (Similar results were obtained for Oil 1.) Also, the initial weights used in the runs shown varied from 305 mg to 320 mg and there, seemed to be no significant influence on weight behavior from this level of variation.

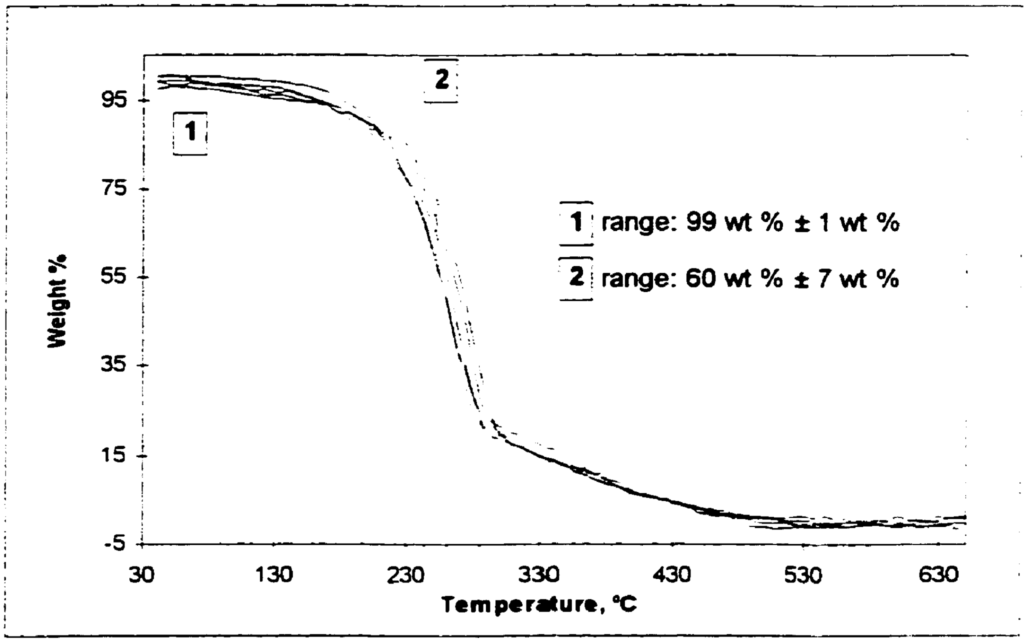


Figure 4.8: Weight Loss Repeatability

4.5.2 Effect of Initial Weight:

Although Oil 2 seemed to show no apparent dependence of initial sample weight on weight behavior for the range of weights used in the study, Oil 1 did show a significant dependence. A plot of three weight curves obtained with different initial weights used is shown in Figure 4.9 with weights of 341, 322 & 314 mg corresponding to curves 1, 2 and 3, respectively. During the initial process, i.e. below ~250°C, and the final process, i.e. >~425°C, the three weight patterns were essentially identical. However, in the remaining region, i.e. 300-400°C, there was a marked difference in the weight behavior. Here, all three curves demonstrated a plateau region that seemed to increase in slope from curve 1 to curve 3. Since the initial weight used decreased from curve 1 to curve 3, there seemed to be a direct relationship between the plateau region and the initial weight of sample used.

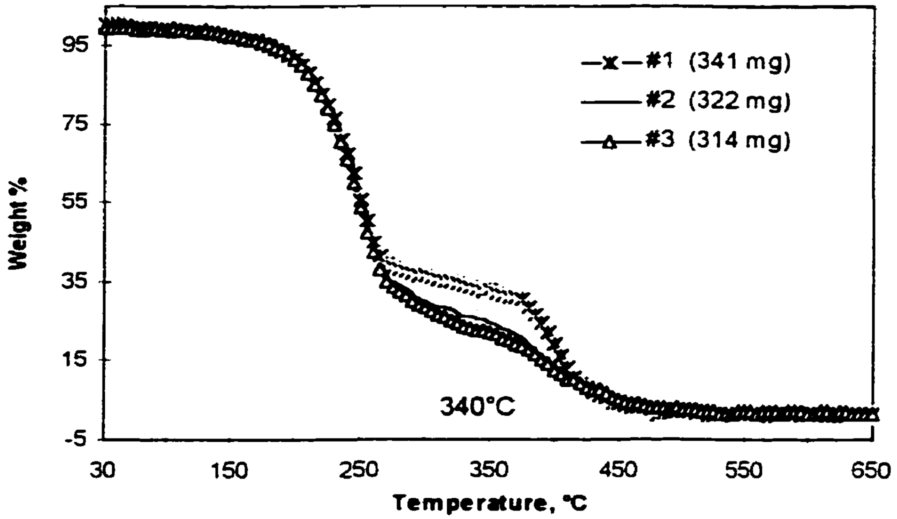


Figure 4.9: Oil 1 Dependence on Initial Weight

In order to attempt to understand and verify this relationship, weight percent readings obtained at 340°C (within the plateau) were plotted versus initial sample weight. The resulting curve is shown is Figure 4.10 showing a clearly linear relationship This suggests that the trend is not a coincidence and that whatever process the oil is undergoing during this temperature region is directly influenced by the amount of initial material. (The explanation for this phenomenon became apparent after further study and is described in detail in a later chapter.)

4.5.3 <u>Thermocouple Placement</u>:

During the course of the study, it was necessary to dismantle the TGA setup for various reasons (e.g. for cleaning purposes). In so doing, it was later realized that the

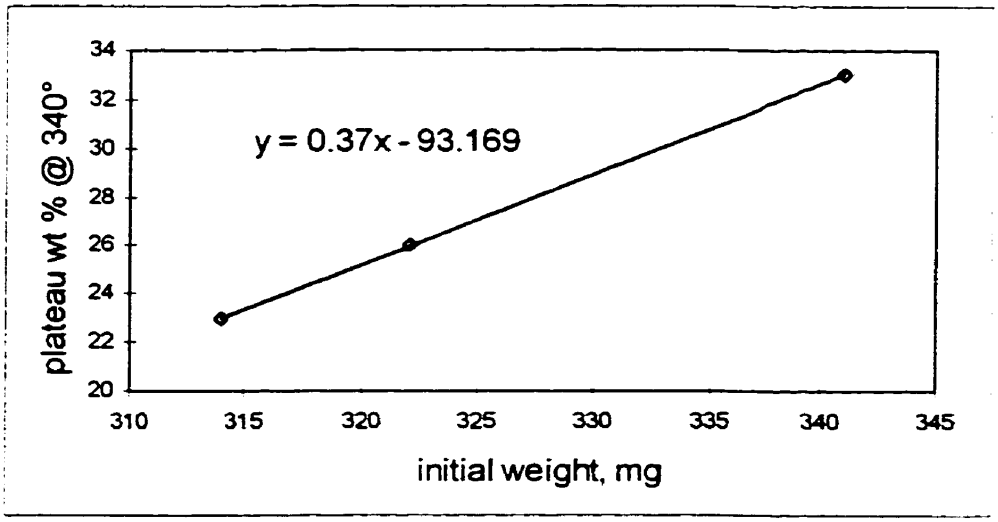


Figure 4.10: Relationship between plateau location and initial sample weight

thermocouple placement in the TGA with respect to the sample container and uniform temperature zone is one of the more crucial parameters to affect repeatability. This effect is explained in Figure 4.11. A change in thermocouple placement in the reactor resulted in a significant shift in the corresponding weight curve (as well as the corresponding FTIR curves). For example, when the thermocouple was placed lower than previously (i.e. from Position 1 to Position 2, as illustrated in Figure 4.11), the corresponding weight curves shifted to the left. For argument's sake, Position 1 is taken as the reference point and is assumed to be within the uniform temperature zone of the reactor, thus giving the proper weight profile, i.e. curve 1. If at a later usage, the thermocouple is placed below the previous position and outside the uniform temperature zone, the temperature of the sample (and the uniform zone) will be higher than the temperature at Position 2, since the maximum temperature in the system will correspond to the uniform temperature zone and therefore, some temperature gradient will exist. This means that something that would occur at a sample temperature of 300°C (with the thermocouple in Position 1, giving the proper weight curve), would now appear to occur at a lower temperature with the thermocouple in Position 2. Thus, lowering the thermocouple results in an apparent shift in the weight profile since it is plotted versus temperature.

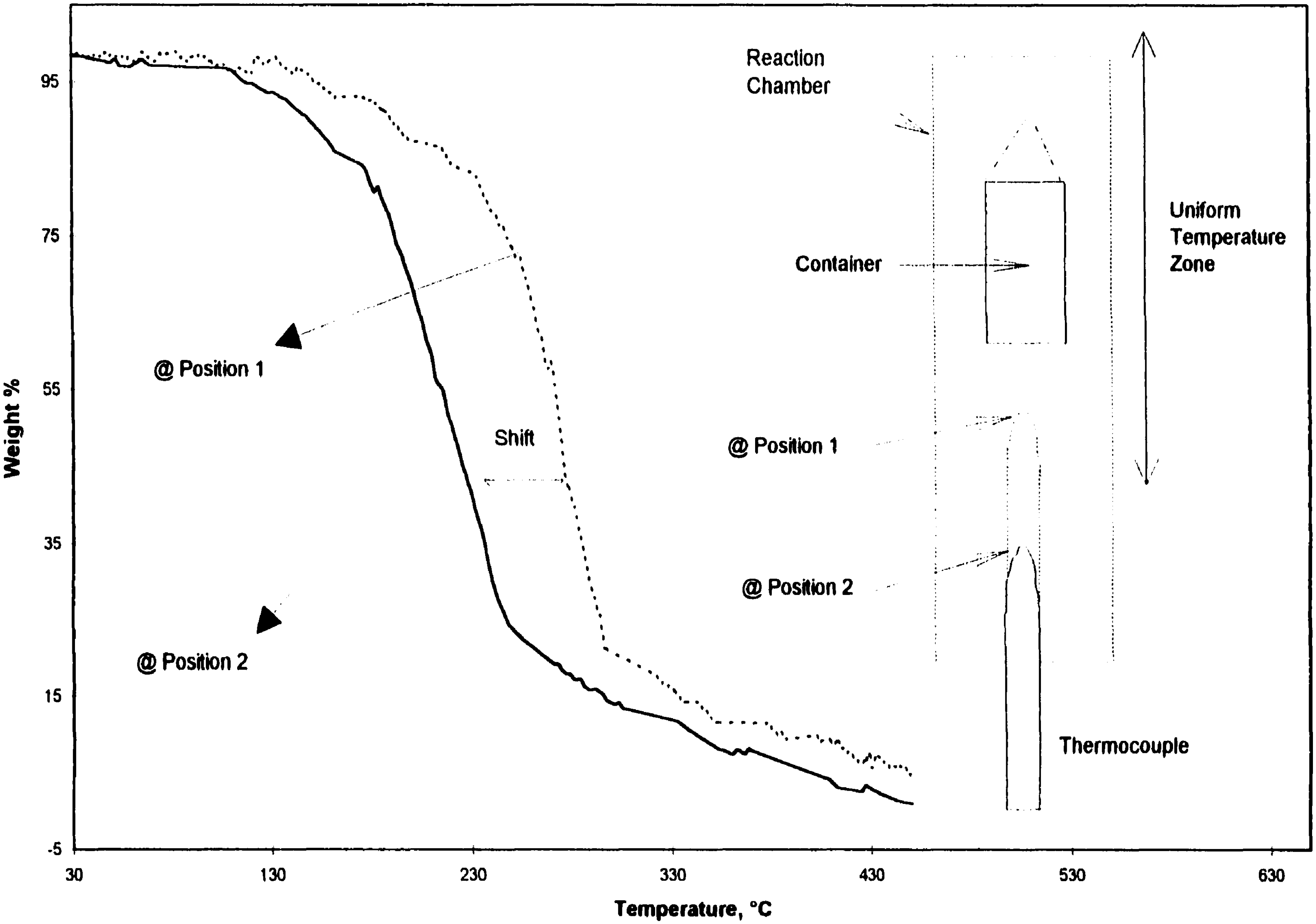


Figure 4.11: Thermocouple Placement Effect

At the beginning of the experimentation process, it was not expected that the process be so sensitive to thermocouple placement and therefore, exact measurements of placement were not taken. However, differences in placement are estimated to be, at most, 1 cm. For this reason, as well as those mentioned above, only runs at which no changes to the setup were made were compared directly. For situations where the setup was changed and a shift occurred, as in Figure 4.11, it is possible to determine the approximate extent of the shift based on the similarities in profiles.

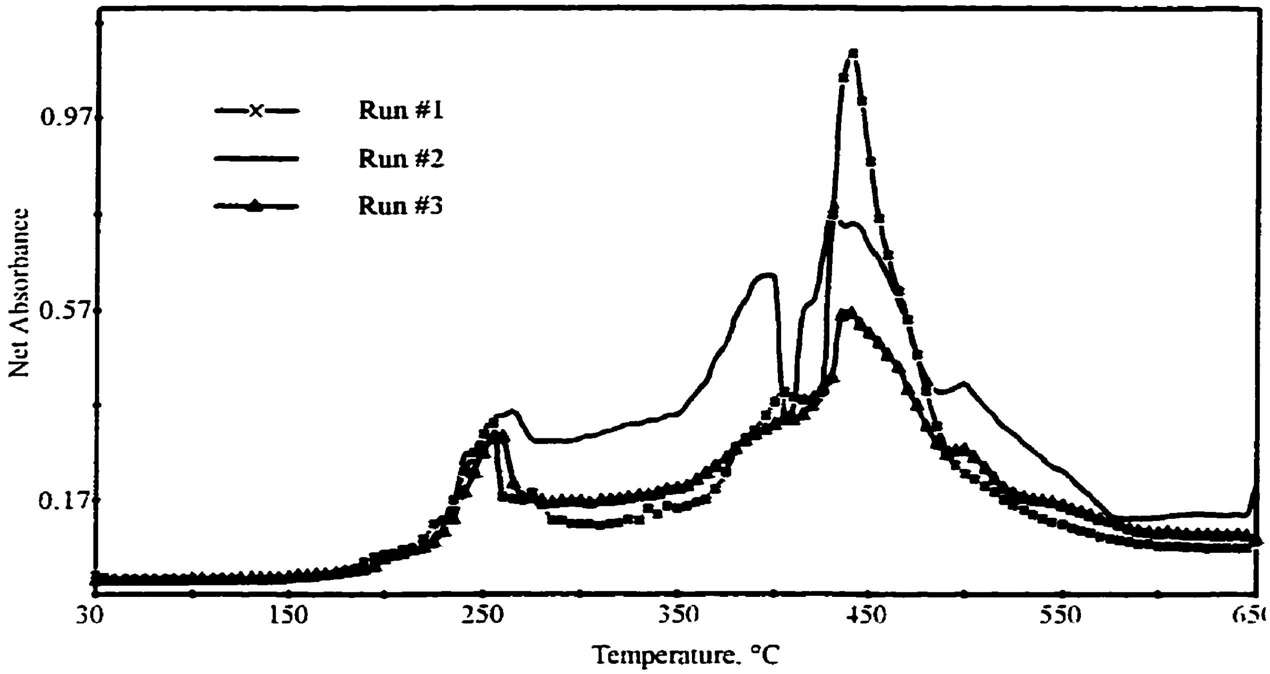
4.5.4 Gas-Phase Evolution:

An indication of repeatability obtained with respect to FTIR results is given in Figure 4.12a & b, where CO_2 profiles are plotted for Oil 1 and 2, respectively. Although there is some scatter, it is clear that the general evolution profile pattern is maintained for both samples. Since it is not within the scope of this work to quantify FTIR data, no comments on the effect of initial weight on the curves could be made and the repeatability is sufficiently good to be able to interpret with respect to temperature. If quantification studies are required, an internal standard needs to be applied to account for the changing FTIR signal intensity which will cause the peak heights to be altered.

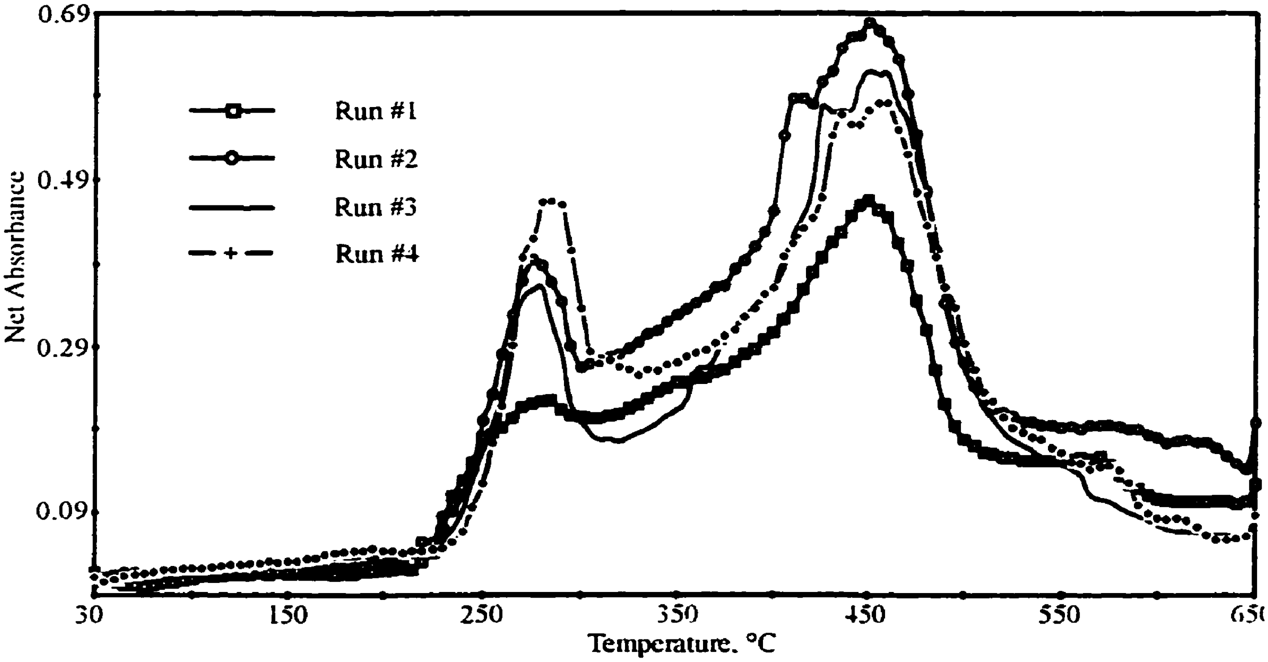
Calibration studies were not attempted since it was necessary to first understand the process before quantifying FTIR data. In this type of combustion-like process, it was expected (and confirmed) that a mixture of compounds be released. In particular, although it could be possible to quantify compounds such as H_2O and CO_2 (with an internal standard such as SF_6 [16,23]), it is quite difficult to quantify the other compounds released. For example, before being able to quantify a particular hydrocarbon, it is necessary to identify exactly what hydrocarbon to quantify. Since this information was not known prior to beginning the project, calibration procedures could not be undertaken.

4.6 Limitations

There are a number of limitations to the study, due to the instrument and the material, that were discovered. One of the limitations already mentioned deals with the combination of sample weight and heating rate that could be applied being limited by contamination of the instrument with condensed hydrocarbons and by balance instability



a) Oil 1



b) Oil 2

Figure 4.12: FTIR Repeatability: CO_2 Profiles for, a) Oil 1 & b) Oil 2

due to rapid release of gaseous compounds. Although the exact nature of the limitation is not understood, it is known that increasing the initial sample size or heating rate would have a tendency to decrease balance stability. Perhaps one parameter can be increased while the other decreased so as to investigate the effect of these two parameters in a larger range. In terms of contamination, the effect of sample size is clear: the greater the sample size, the greater the condensation, for a specific heating rate. However, it is not known how heating rate affects the contamination phenomenon. It is most likely that an increased heating rate would reduce condensation since the sample would have less time to generate the condensing substance prior to the furnace temperature being high enough to oxidize the substance within the uniform temperature zone.

Despite the heating rate used, the sample generates vapors that deposit on various parts of the system. In terms of balance stability, this causes noise in the balance through electrostatic forces and reduces precision. This makes runs progressively noisier and makes zeroing of the balance more difficult (affecting accuracy). Despite this limitation, the balance noise (~ 4 mg) was considered acceptable for the purposes of this work. For future work, it will be necessary to periodically clean the instrument to reduce static buildup and thus reduce balance noise (and increase accuracy).

The condensation which is produced also affected the FTIR data collection after 650°C. The bottom of the reactor tube where the condensed material collected became hot enough after an oven temperature of 650°C to vaporize or oxidize the condensed matter. This resulted in artifact peaks in the FTIR spectra to appear. In this study, the gas phase process is over by this temperature and thus, the artifact peaks do not hinder the study. However, this limitation may need to be dealt with in future work.

Another limitation of the instrument that had to be considered when analyzing results dealt with the FTIR transfer line. The line is heated to reduce condensation of hot combustion gases. However, the maximum temperature of the transfer line materials only permit a temperature of 300°C. As was mentioned previously, the oil sample studied generates easily condensable materials and thus it is most likely that some hydrocarbons are condensing within the line and thus do not make it to the FTIR sample cell. This means that the data collected with the FTIR probably does not include much information on materials that condense at temperatures below 250°C, the temperature the transfer line is heated to. Again, for the objectives of this study, this limitation was not detrimental since general process behavior could still be observed. The evolution profiles generated in the gas phase are for CO_2, CO and hydrocarbons which will not condense at this temperature and the PAH gas-phase study undertaken circumvented the transfer line.

Finally, there is a limitation based on the method of producing the evolution profiles that must be kept in mind. The curves were all generated at 5°C intervals and thus any subsequent temperature ranges determined from these profiles are, at best, accurate to within 5°C. Therefore, as is evident in some cases, the assigned temperature of a zone may not seem to correspond to the curve exactly. This is because the determined temperature must be rounded to the nearest 5°C. However, this level of accuracy did not deter the ability to properly interpret the data collected.

Chapter 5: Physical and Chemical Properties of Oils Studied

Two used lubricating motor oils were studied and are referred to as Oil 1 and Oil 2. Prior to submitting the two oil samples through the combustion process, it was necessary to determine selected physical and chemical properties in order to attempt to explain observed oil behavior during combustion. On a visual basis, there appeared to be no difference in the samples and neither seemed to have any inclusions. The two samples were analyzed (at Galbraith Laboratories, Knoxville, TN) for their Ultimate and Proximate contents and the results obtained shown in Table 5.1.

Table 5.1: Used Oil Properties (as received)

Analysis	Oil 1	Oil 2
Ultimate Analysis:		
C, wt %	83.70	83.95
H, wt %	13.40	13.11
S, wt %	0.54	0.35
N, wt %	< 0.5 *	0.16
O, wt %	< 0.5 *	2.41
moisture, wt %	0.0829	0.33
ash, wt %	0.86	0.47
chlorine, wt %	1.12	0.0091
Proximate Analysis:		
fixed carbon, wt %	0.3371	0.45
volatile matter, wt %	98.72	98.75
ash, wt %	0.86	0.47
moisture, wt %	0.0829	0.33
Others:		
heating value, kJ/kg	44776 #	44140
density, kg/L @15°C	N/A	0.8732

* Below Detection Limit
\# Calculated

Since the two oils are used in the same type of process (namely as engine lubricant), the major properties are expected to be very similar and, as expected, the two oils have very similar properties. As can be seen in Table 5.1, the major properties for the two oils, namely carbon, hydrogen and volatile matter, are essentially the same. Both oils comprise almost 84 wt % carbon and contain about 99 wt % volatile matter. There are some properties, such as water and ash contents, that vary only slightly between the two oils. Of the hydrocarbons present, a typical lubricating oil comprises about 70% paraffinic compounds (as was noted in Table 1.3). Since the properties are similar, the heating values of the two oils are also expected to be similar. The Oil 1 heating value was calculated[24] to be slightly higher than for Oil 2, which is due to slightly more H content. Neither oil has a significant amount of sulfur which means that not much SO_x is expected to be released during the process. Similarly, neither oil has significant amounts of nitrogen so that not much fuel NO_x is expected either. Also, since the process temperature is low (<1000°C), not much thermal NO_x is expected.

Since the difference in behavior of the two oils was studied, the main interest was in the oil properties that are different. The properties where the two oils differ are in sulfur, oxygen, water, ash, chlorine and fixed carbon (non-volatile organic material[25]) contents. The most significant differences are believed to be in the oxygen, chlorine and water contents (significant with respect to the burning process). Oil 2 contains less sulfur, chlorine and ash but contains significantly more oxygen and water than Oil 1. The most important property is the oxygen content since the process being studied involves oxidation of hydrocarbons and it is anticipated that there be some measurable/noticeable differences in the areas of the process being studied due to the difference in oxygen content. (If this is indeed the case, it will add to the knowledge we can gain from our approach to the study of the process.) Oil 1 contains very little, if any, oxygen (i.e., below detection limit), while Oil 2 contains 2.41 wt% elemental oxygen.

Chapter 6: Behavior of Sample Weight

6.1 Temperature Resolved Weight Behavior

The first aspect of the process studied was the weight behavior of the two oils. A weight loss is anticipated due to oxidation and heating of the sample. The manner (i.e. rate and temperature ranges) in which the weight loss manifests itself gives insight into the events taking place during the heating period.

Representative weight loss curves were selected for comparison from the runs performed on each oil. The curves selected are shown in Figures 6.1 & 6.2, plotted as sample weight percent versus furnace temperature. Since different weight loss events are evident (by the general slope of the weight loss curve), the heating process can be separated into different zones, based on these curves. The zones include information on temperature, weight loss and average rate of weight loss. (Note that since a small sample size is utilized and the thermocouple is placed close to the sample container, it is assumed here that the sample temperature is uniform and equal to the reactor temperature. However, during combustion events, the exothermicity of the event would probably result in a local high temperature region which should be quickly dissipated.) Due to the constant heating rate used in this temperature range (30-650°C), temperature that is plotted in Figures 6.1 & 6.2 is essentially equivalent to run time. Since the heating rate used was 3°C/min, every 3°C interval on the curve corresponds to 1 minute.

Although weight data were collected throughout the entire heating process (i.e., up to 1000°C), it is clear from the curves in the figure that, by 575°C, no further significant weight loss was observed (i.e., any further weight loss is indistinguishable from balance noise since very little sample remains at this point). Therefore, the curves shown to compare weight loss behavior in the two oils are only plotted up to 575°C.

6.2 Oil 1: Zone Designation and Discussion

When Oil 1 was subjected to the conditions described above the behavior was very repeatable (as was shown in Figure 4.9). A representative curve, shown in Figure 6.1, shows the weight of the sample (in terms of weight %) as a function of temperature.

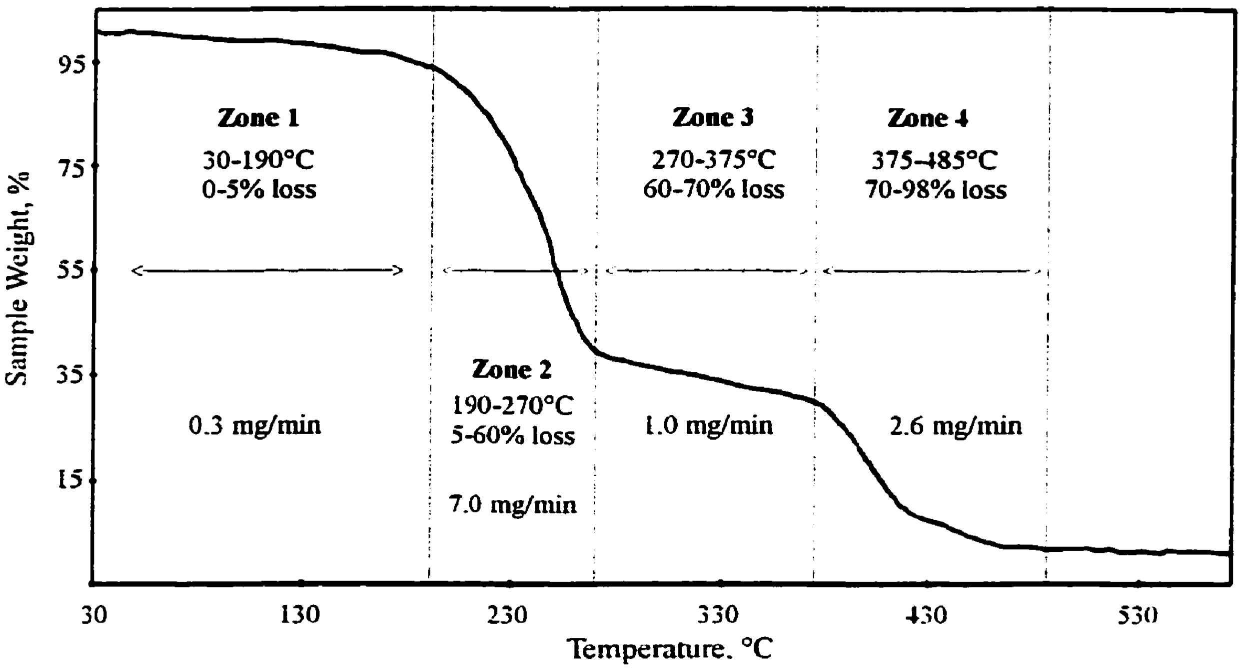


Figure 6.1: Weight Behavior of Oil 1

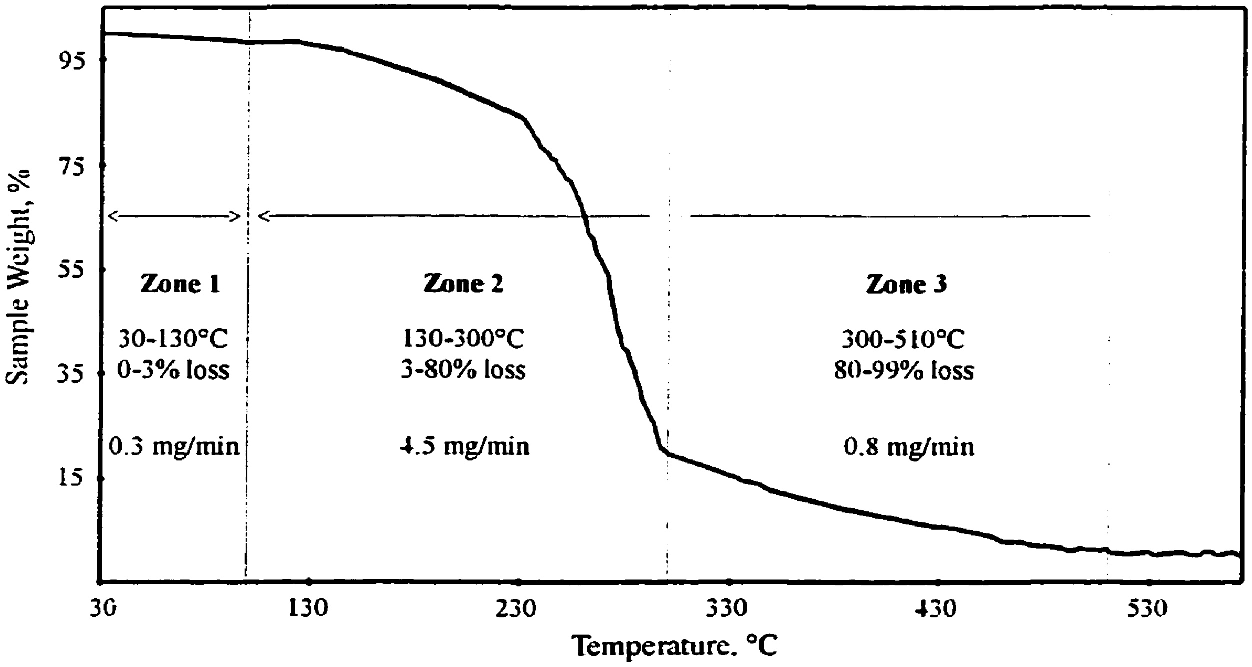


Figure 6.2: Weight Behavior of Oil 2

Based on this weight behavior, the process can clearly be "broken up" into four distinct zones. The first zone is one where slow weight loss occurs. This weight loss is due mainly to the release of very volatile materials such as light hydrocarbons, presumably paraffinic because of lube oil makeup (see Table 1.3), as well as any water present and is characterized by a 5% mass loss from room temperature to 190°C. When heating rate and initial sample weight are factored in, this works out to an average rate of weight loss of 0.3 mg/min (which was calculated by dividing the weight loss, in mg, for the zone by the time equivalent for the zone). Zone 1 is followed by Zone 2 which is characterized by a very rapid weight loss (compared to the first zone). This zone goes from 190°C to 270°C. In this period, the sample loses weight from 95% to 40% or 5% to 60% cumulative loss (i.e. the sample loses half of its weight during this period compared to only 5% in Zone 1) at an average rate of 7.0 mg/min (i.e. over 20 times faster than Zone 1). Since the sample is mostly liquid, it is expected that this zone be dominated by volatilization of some of the oil components, mainly volatile paraffinic hydrocarbons, with limited oxidation occurring as well. Some of the vaporized hydrocarbons will react with the oxygen present in the reaction air while still in the Uniform Temperature Zone, thus producing CO_2.

Zone 3 comprises the region between 270°C and 375°C. In this zone, the sample weight only decreases from 40% to 30% in a temperature range of 105°C, (from 270°C to 375°C). Therefore, it can be seen that the rapid weight loss seen in Zone 2 (7.0 mg/min) is followed by a slow weight loss region, at a rate of 1.0 mg/min. It is believed that in this region, there is a transition from a liquid to solid and the oxidation process slows down until a sufficiently high temperature is reached to continue the process. The leveling off of the weight loss curve leads to the possibility that there is an oxygen limiting step taking place in the process. In other words, the rate of the process has shifted from one dominated by kinetics which are faster, to one dominated by diffusion of oxygen to the sample from the reaction air.

In Zone 4, the process again shows a relatively rapid weight loss from 375°C until the end of the Zone at 485°C. This zone is characterized by an average rate of weight loss of 2.6 mg/min (about 3 times as fast as the previous). The sample weight loss is essentially over by 485°C, after which any further weight loss would be hidden in the noise of the instrument balance. The weight remaining at this point is about 2 wt% and would consist of inorganic matter and perhaps some yet unburned hydrocarbons. In this final zone, it is believed that the remaining volatile material trapped within the solid, charry material, is being oxidized, since the temperature is sufficiently high to do so.

6.3 Oil 2: Zone Designation and Discussion

When the Oil 2 weight loss curve was sectioned in the same manner as for Oil 1, only three Zones were obtained (as shown in Figure 6.2). The initial zone was one in which a very small weight loss occurred over a significant temperature range. In this zone, Oil 2 sample lost only 3 % of its weight from 30°C to 130°C which worked out to an average rate of weight loss of 0.3 mg/min (which is the same obtained for Oil 1).

Zone 2 followed, characterized by a more rapid average rate of weight loss, at 4.5 mg/min (i.e. 15 times faster than Zone 1). This zone occurred between 130 & 300°C and resulted in the sample losing 77% of its weight. It is clear that the sample loses the most significant amount of its weight in this region and it is believed that the major process involved is the loss of the volatile hydrocarbons (probably paraffinic) found in the sample.

The final zone for Oil 2 (i.e. Zone 3) sees the sample losing the remaining 19% of its weight between 300 and 510°C. This works out to a much slower rate than in the previous zone, namely 0.8 mg/min (which is also less than Oil 1's average rate of 2.6 mg/min in the final weight loss zone).

6.4 Weight Behavior Comparison

If the two weight behaviors are compared, it is clear that the two curves exhibit some similarities (which is to be expected since the major oil properties are similar). Up to a temperature of about 250°C, a similar behavior is revealed. Both oils underwent an initial period of little weight loss (Zone 1) followed by a period of significant weight loss (Zone 2) where the majority of weight loss occurred in both oils. However, after this temperature (i.e. 270°C), there is a significant difference in the two oils. Oil 1 exhibits a drastic slow down in the weight loss process, forming a plateau region in the weight loss curve. Conversely, for Oil 2, the weight loss process does not seem to be disturbed in a similar manner. Since Oil 1 is the sample having a limited amount of elemental oxygen initially, the process slow-down could be attributed to an unidentified event taking place where the amount of oxygen needed for oxidation is severely limited. (Perhaps, this slow down has something to do with the sample becoming more solid.)[19]

Finally, the last weight loss event (Zone 4 for Oil 1 and Zone 3 for Oil 2) completed the weight loss of the sample. Although the process was studied up to 1000°C, it is clear that under these conditions, the sample weight loss in both cases was essentially over by 650°C, where over 98% of sample weight has been lost.

6.5 Process Kinetics

Weight data obtained during constant heating rate experiments using a TGA can be used to study overall process kinetics. Weight loss kinetics during combustion are complicated by the simultaneous reactions occurring involving a number of different compounds, especially during the combustion of oils[19]. Therefore, this type of kinetic study, which has been previously performed[19], accounts for bulk changes in the system.

An Arrhenius-type equation describing the overall reaction kinetics is assumed. This model assumes also that the rate of weight loss of the entire sample depends only on the rate constant, the remaining sample weight and the temperature of the sample. A typical assumption of first order kinetics is made[19], leading to the following equation:

$$(dM/dt) = A_r \exp(-E/RT)\, M \qquad (6.1)$$

where (dM/dt) is the rate of weight loss of the sample (obtained from the TGA data and is equivalent to the derivative of the weight curve), M is the current weight, A_r is the Arrhenius constant (s^{-1}), E is the activation energy (kJ/kmol) and T is the sample temperature, in K, (which is assumed to be equal to the TGA furnace temperature). R is the ideal gas constant and has a value of 8.315 kJ/kmol K. Rearranging the equation, the following form is obtained:

$$\log [(dM/dt)/M] = \log A_r - E/(2.303RT) \qquad (6.2)$$

By plotting log [(dM/dt)/M] versus 1/T, a straight line would indicate that the kinetics are indeed first order. If so, the slope of the plotted line would yield the overall activation energy.

The above described kinetic analysis was applied to the weight data obtained from each oil and the results are described here. It must be noted that previous experiences with applying this method to oils in air in a TGA had encountered some difficulties in terms of accuracy of the activation energy determined[19]. Since oxidation reactions are typically exothermic, the temperature of the sample is most likely higher than the furnace temperature. Furthermore, the temperature increases are typically sudden which cause instability in the weight curve obtained. Therefore, it was decided to not attempt to determine values for kinetic parameters such as activation energy for this study. However, other information about the process (such as determination of reaction zones) may be forthcoming by applying the kinetic model to the two oils being studied.

The results obtained in this study are shown in Figure 6.3 & 6.4 for Oil 1 & 2 respectively, where the plots obtained for each oil studied are shown. It was found that different parts of the oxidation process studied for both oils could be described by different first order kinetics parameters (i.e., different groups of chemical reactions dominating each region). This is similar to what has been previously found for crude oils[19]. However, since the samples studied here are lubricating oils, the temperature ranges found are different.

Oil 1 shows 4 distinct regions where the overall process is approximately governed by first order kinetics. These regions are similar to the weight loss zones designated in Figure 6.1 which were designated on the basis of weight curve pattern. A comparison between the two process designations is shown in Table 6.1. Although there are some slight differences in the two temperature ranges, the comparison confirms that the previous zone designations and explanations were reasonable.

Table 6.1: Comparison of Oil 1 Kinetic Regions and Weight Zones

Zone	Kinetic Range, °C	Weight Range, °C
1	100-155	30-190
2	192-242	190-270
3	278-338	270-375
4	375-434	375-485

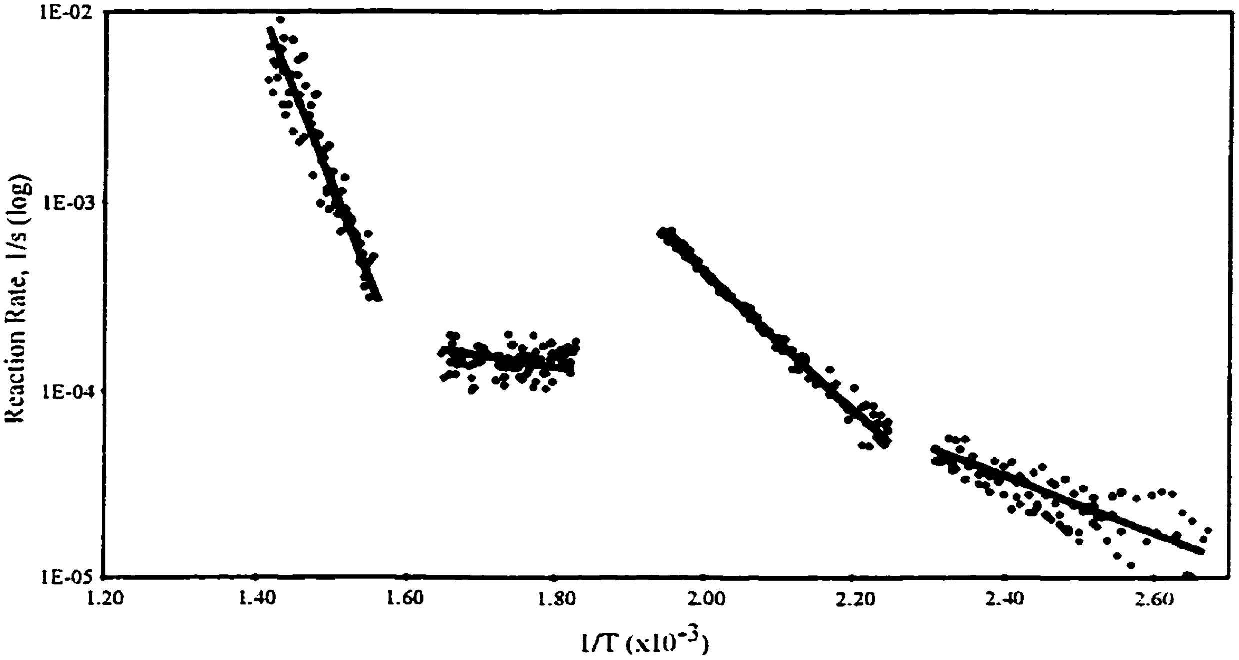


Figure 6.3: Oil 1 Kinetics Results

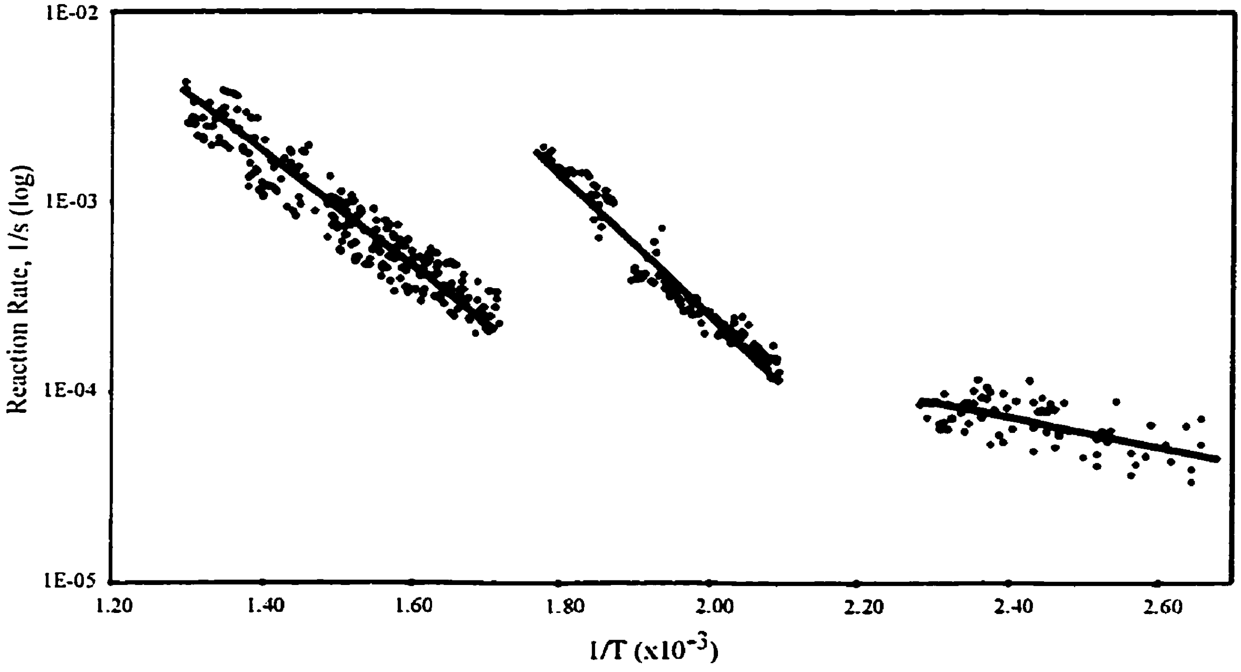


Figure 6.4: Oil 2 Kinetics Results

The kinetic results on Oil 2 show only three distinct regions where the kinetics are first order. This is similar to the three zones designated based on the weight behavior of Oil 2 (see Figure 6.2). A comparison between the two temperature ranges is shown in Table 6.2 below. In the case of Oil 2, the ranges are not in as good agreement as they were for Oil 1, since the kinetic analysis does not account for transition between regions. However, the ranges are approximately similar.

Table 6.2: Comparison of Oil 2 Kinetic Regions and Weight Zones

Zone	Kinetic Range, °C	Weight Range, °C
1	106-166	30-130
2	210-287	130-300
3	322-500	300-510

In studies involving crude oils, three distinct regions in the temperature range were found where first order kinetics described the overall process (each region having a different set of parameters)[19]. Each region was therefore, associated with a different aspect of the process (i.e., different types of reactions dominating).

Another similar method was utilized to study solid carbonaceous material in a TGA setup[26]. This study looked at reaction speed in order to determine ignition temperature of the material, although the process being studied is more like a pool fire phenomenon due to the surface flame expected rather than a typical combustion process. Since the TGA setup does not allow for observation of the sampled during the heating process, an alternative method for determining at which point, if any, there is ignition of the sample occurring is necessary. This method was based on conversion of the sample and defined reaction speed, α, as the following:

$$\alpha = (dM/dt) / M_o \qquad (6.3)$$

This approach is similar to the kinetics approach except that the rate of weight loss, dM/dt, is divided by the initial sample weight (M_o) and not the current weight (M) (a difference brought about by defining the system model in terms of sample conversion). In this way, it is assumed that the process has reached an ignition point when the reaction speed is greater than 5×10^{-4} s^{-1} (it is also assumed here that the rate threshold utilized for solid particle ignition also applies to liquid)[26]. When this approach was applied to see if an ignition temperature could be determined on this basis, the results obtained are shown in Figure 6.5 & 6.6 for Oil 1 & 2, respectively. The plots consist of the reaction speed and sample weight versus temperature.

Each oil studied generated two maxima in the reaction speed curve, corresponding to major weight loss events. For Oil 1, according to the ignition threshold, ignition takes place only during the first peak and first occurs at approximately 239°C. The ignition process lasts until a temperature of 249°C, which is approximately 3 minutes. For Oil 2, both peaks in the reaction rate curve cross the ignition threshold, suggesting that two separate ignitions take place during the process. The first ignition takes place at 271°C and lasts longer than the similar one obtained for Oil 1 (i.e., almost 7 minutes) and is probably due to the combustion-like characteristics of the process. The second ignition temperature for Oil 2 is at 408°C but only lasts about one minute and may be associated with the oxidation of char.

The results obtained in the ignition study seem to be reasonable. However, in the studies currently undertaken, it was not possible to confirm if ignition (in terms of flame) actually took place. It is important to confirm the ignition analysis with physical evidence of ignition, especially in the case of Oil 2. The second ignition temperature was not expected since the corresponding weight loss in this part of the process is not significant. This part of the process is associated with char oxidation and since Oil 2 contains internal oxygen, it could be expected that the char oxidation be sufficiently rapid as to cause ignition. However, it is also possible that scatter in weight readings occurs due to random error in the balance system which would manifest itself as a ghost peak during the ignition analysis.

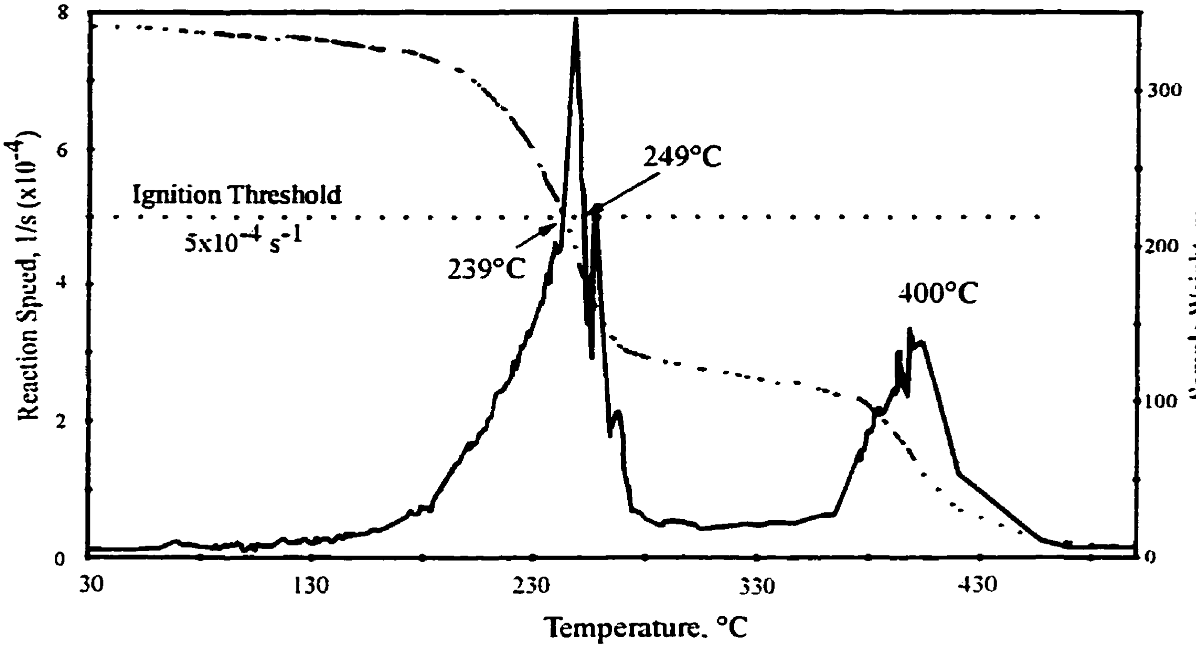


Figure 6.5: Oil 1 Ignition Determination

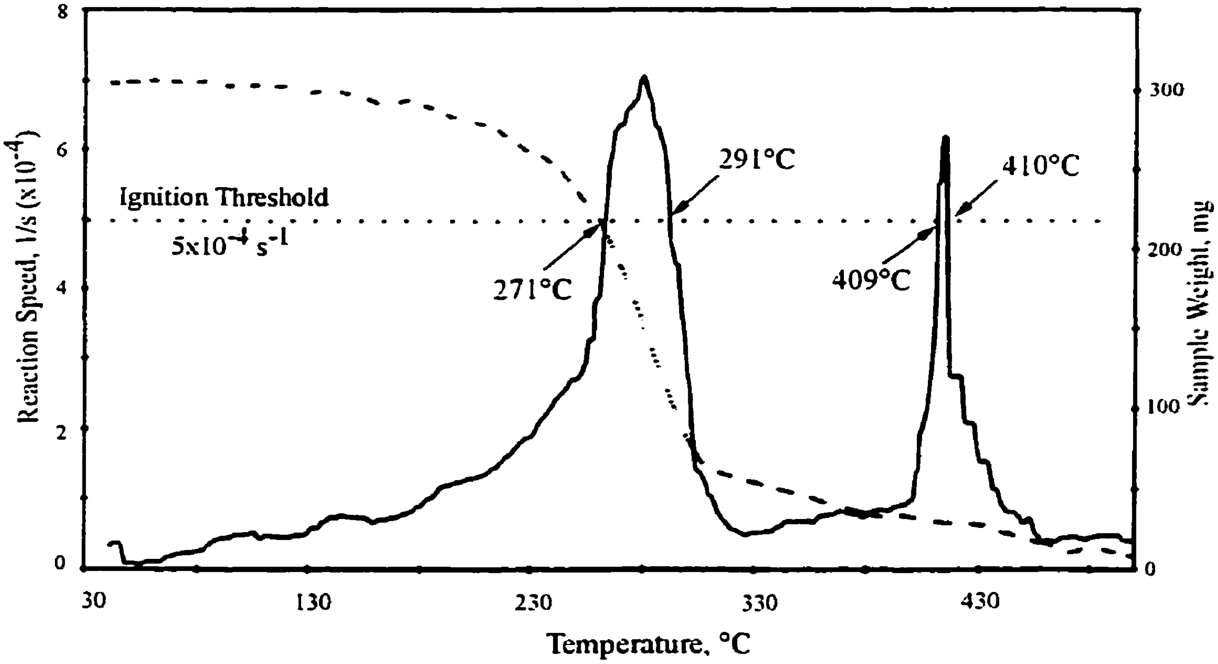


Figure 6.6: Oil 2 Ignition Determination

Chapter 7: Gas-Phase Product Evolution

Based solely on the weight loss curves, it is only possible to hypothesize as to the changes taking place to the sample. In order to gain further information on those events (in order to formulate a stronger and better-supported hypothesis), the evolution of typical combustion gas by-products were studied and compared.

In conjunction with the weight loss behavior of the sample during the process, gas-phase profiles of the major components were generated (a process known as Evolved Gas Analysis). This was done only by plotting the net absorbance (obtained from the FTIR) of peaks representing different compounds against furnace temperature. An example of a typical spectrum obtained from the FTIR during the process was shown in Figure 4.4 with different compounds (i.e., H_2O, HC, CO_2 and CO identified). The figure can be used to demonstrate how the gas phase evolution profiles were generated. If CO_2 is taken as an example of how this is done, the height of the peak less the absorbance of the baseline gives the net absorbance which is plotted against the temperature the spectrum is taken at.

The Evolved Gas Analysis profiles generated were for typical combustion products; CO_2, CO and total hydrocarbons (HC). The wavelengths used to generate these profiles were 2356 cm^{-1} for CO_2, 2183 cm^{-1} for CO and 2934 cm^{-1} for HC. (Note that for hydrocarbons, it was not possible to identify individual compounds with the FTIR since different types of hydrocarbons are released at the same time. However, the evolution of HC reflect the characteristics of the reactions taking place.[27])

In all cases, the carbon monoxide profile followed the same shape as the carbon dioxide profile, as is shown in Figure 7.1. The figure shows how the CO peaks have the same pattern as the CO_2 peaks but with a much lower intensity (which probably accounts for the slight discrepancy in maximum peak temperature of 5°C). This pattern was consistent for all runs and for both oil samples. Because the CO profile resembled the CO_2 profile, it only served to confirm the presence of CO_2 by showing that some partial oxidation was indeed taking place (i.e., the presence of CO allowed us to confirm that the peaks in the region were indeed mainly CO_2 and not due to some other component). In terms of understanding the events taking place for the two oils, which is the goal of this

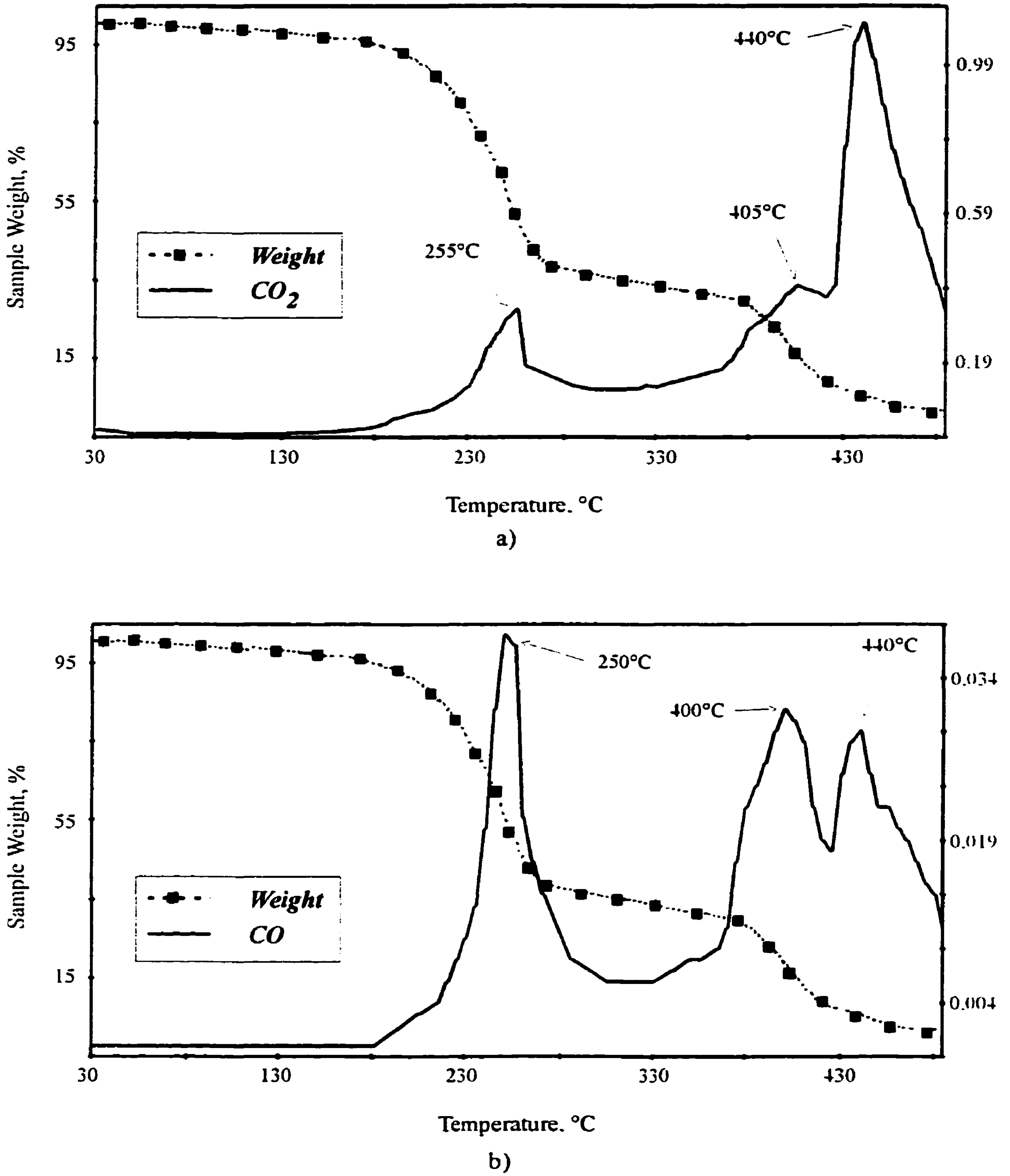


Figure 7.1: Gas-Phase Profiles of Same Run for a) CO_2 & b) CO

particular exercise, the evolution pattern of CO provides no insight into the process that cannot be gained by the CO_2 profiles. Therefore, further figures will be limited to only CO_2 and total hydrocarbon profiles.

CO_2 and HC evolution profiles were generated for both oils to understand the events taking place causing the weight profiles seen. The results obtained are shown in Figure 7.2 (with the weight loss profile plotted as a reference). As was previously seen in the weight behavior, the evolution profiles after 650°C were also generally flat. For this reason, the profiles were only plotted for the respective temperature ranges of interest (i.e. 30-500°C since little pertinent information is available after 500°C). Note that the gas phase data is plotted as net absorbance since it is not possible to compare two runs directly and quantitatively unless a calibration procedure is undertaken (as was explained in Chapter 4).

In both cases, the gas phase results show that in the initial zone (below ~190°C), which is characterized by minor weight loss (<5%), essentially very little occurs during the heating and oxidation processes. Due to the low temperatures, one would expect this behavior in terms of gas phase release. Since there is only a total of approximately 5% weight loss over a large time period (about 50 minutes) in this zone, it was not expected to see very high amounts of any of the components.

However, in the following major weight loss region (corresponding to Zone 2 for both oils, having temperature ranges of 190-270°C & 130-300°C for Oil1 1 & 2, respectively), the process is dominated by the release of a significant amount of hydrocarbons in both cases (as is seen by the three HC peaks at 225°C, 250°C and 275°C for Oil 1 and the single peak at 280°C for Oil 2). There is also the presence of limited carbon dioxide formed in this Zone (peak at 255°C for CO_2 for Oil 1 and 280°C for Oil 2), signifying oxidation taking place. Although not specifically shown here, the presence of CO in this region and its similarity to the CO_2 profile confirm that partial oxidation is also taking place in this part of the process. The evolution profiles seen in Figure 7.2 would suggest that, in this part of the process, the event dominating is the volatilization of liquid hydrocarbons in the oil sample (which would still be liquid at this point).

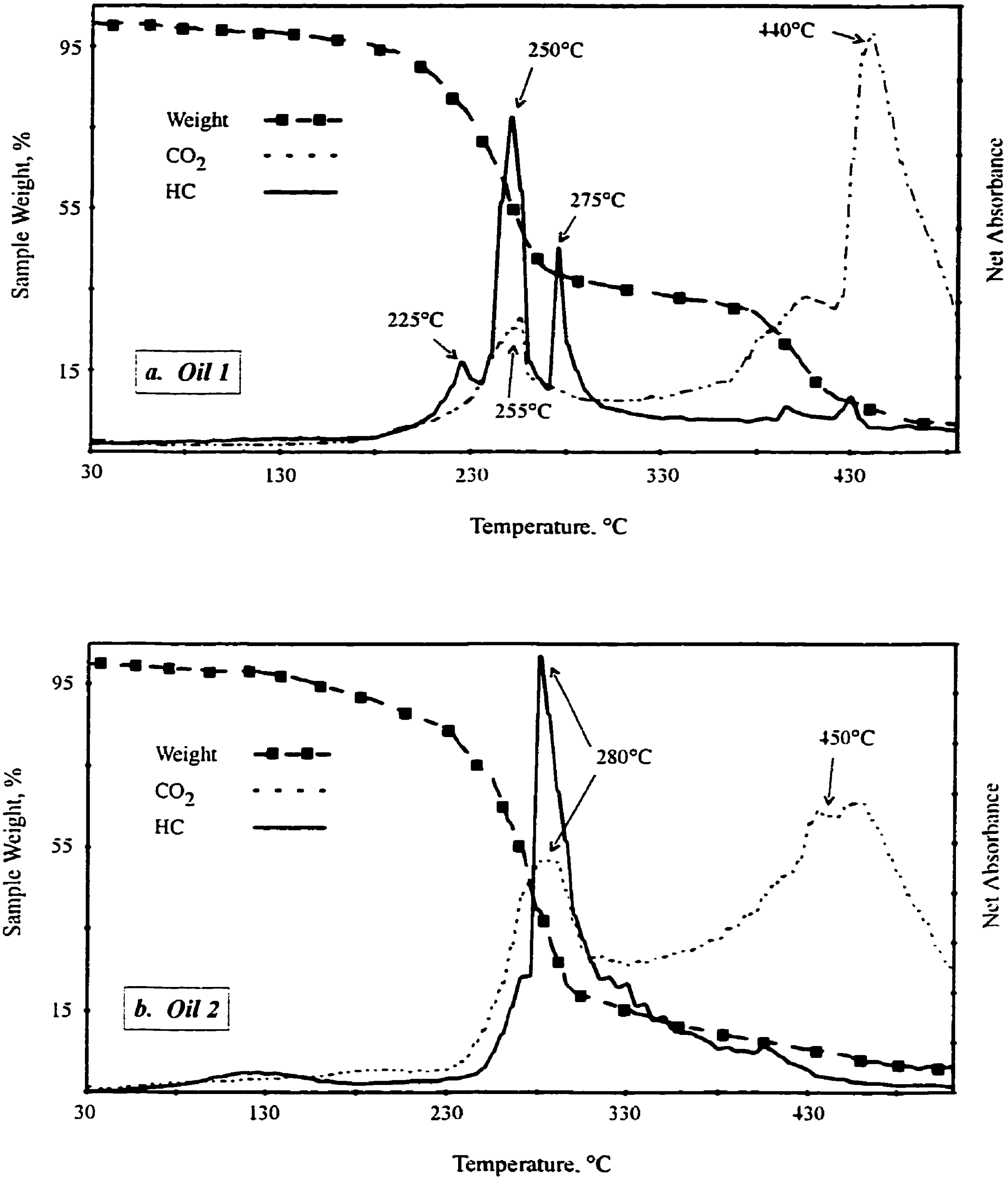


Figure 7.2: Evolution of Combustion Gases for a) Oil 1 & b) Oil 2

The final weight losses (Zones 4 & 3 for Oils 1 and 2, respectively) are dominated by the formation of CO_2 (with a generally wider peak found at 440°C for Oil 1 and 450°C for Oil 2) with a less significant hydrocarbon release. This behavior indicates that the process taking place in this temperature region is dominated by oxidation rather than simple release of hydrocarbons (or volatilization). This behavior would be consistent with having solid particles remaining in the container, still having some hydrocarbons that are being oxidized. That is, the hydrocarbons still present within the particles are burned in this zone. It is believed that at this point in the process, the sample has become solid and is continuing to oxidize as the temperature increases. Since the hydrocarbons would be trapped within the particle, their simple release into the atmosphere would be delayed (since the hydrocarbons would have more difficulty diffusing out of the particle). As the hydrocarbons get to the surface, they burn off, but not completely, since there was also evidence of limited CO presence. Due to this delay, in conjunction with the higher temperatures found in this part of the process (i.e., >400°C), the conditions are such that most of the hydrocarbons released will have the time to be oxidized. It is consistent with the evolution profiles generated since both oils show the domination of carbon dioxide formation with very little hydrocarbon release. It suggests that solid particles were indeed present in this part of the process and the lack of significant amounts of HC peaks in this zone supports it.

Oil 1 had an extra zone in comparison to Oil 2 which is a transition zone between the Zone 2 and Zone 4 weight losses. The transition zone for Oil 1 (between 270 and 375°C) is characterized by a drop in both CO_2 and hydrocarbon release, signifying that the event previously taking place (i.e., liquid hydrocarbon volatilization) is stopping and the process is undergoing some kind of liquid/solid transition while slowing down considerably. It is believed that the hydrocarbon peak at 275°C is just a carry-over from Zone 2 hydrocarbon release. Towards the end of this plateau region, the amount of CO_2 present begins to increase, signifying that the limitations to the process are beginning to be overcome by this point in the heating process and may signify some sort of breakthrough occurring which is to be explained in Chapter 9.

Chapter 8: Solid Residue Behavior

8.1 Introduction

In addition to the understanding of the evolution of gases presented in the previous Chapter, it is also important to understand how the solid particles are formed during the waste oil combustion process. The understanding of solid particle evolution is important in terms of determining process parameters that influence final particle properties so as to obtain a final residue having properties conducive to safe disposal. The sampling of the residue was done by stopping the heating process at a desired temperature in order to collect the residue remaining at the bottom of the sample container.

Although the bulk of the weight loss and vapor phase of the process is complete by approximately 650°C, it is not expected to be the same for the solid residues since some combustible material will still remain at this temperature. The amounts of combustible material remaining will be less than that which can be detected by the balance system and thus, no further weight loss is seen. (This is due to the small initial sample which means that by the time the sample has passed the transition stage, the mass remaining is small enough so as to approach the balance detection limit.) Although neither the FTIR nor the TGA would detect changes occurring in this part of the process, changes to the solid residues take place nevertheless.

At some point in the heating process, the liquid sample becomes solid and an attempt was made to observe the solid behavior after the transition by looking at solid morphology. It is important to understand this part of the process since a solid residue is generated in combustion processes which will require disposal. The characteristics of the residue will give us insight as to its potential environmental impact upon disposal.

The most important thing to know is the characteristic properties of the final residue (i.e. at 1000°C) since the heating process is only carried out to this temperature and this would be the material eventually disposed. However, it is also important to understand the processes that ultimately result in the final residue properties. Only once the processes are understood could there be likelihood of control in order to alter particle evolution in a desired way to facilitate final disposal. Therefore, in order to understand the residue behavior leading up to the final temperature, the process was stopped at 400°C, 650°C as well as 1000°C to collect solid samples (following the transition from liquid to solid) and the surface of the particles collected were observed using a Scanning Electron Microscope (SEM), at magnifications of up to 700 times the actual size. By observing the morphological evolution of the solid particles, it is hoped to be able to understand the physical and chemical processes that the particles undergo during the heating process from 400°C to 1000°C.

8.2 Confirmation of Oil Liquid/Solid Transition Phase

The first step of the solid-phase analysis was to identify the temperature region where the sample transformed from liquid to solid. Since the heating process is quite slow, this transformation is expected to occur in a measurable/significant temperature range (when compared to a typical combustion process) which will allow for its observation. It was hypothesized that this transition zone involved a tar-like sample and that the subsequent part of the process involved solid oxidation. Confirmation of this hypothesis was to be accomplished visually; however, for purposes of presentation, images of the residual material were taken by optical microscope. Based on observations made previously, i.e. on weight and gas-phase behaviors, a most likely temperature range that the transition phase would be found would correspond to Oil 1 Zone 3 (i.e., the plateau region between 270°C and 375°C, shown in Figure 6.1) due to the expected limitation caused by the lack of internal oxygen present in this oil. Therefore, the heating process was stopped at 300°C for both oils (which falls within the Oil 1 plateau region) and the sample characteristics observed. Although no such plateau exists for Oil 2, it was believed that the same approximate temperature ranges and processes occurred for this oil as well and that a similar type of sample phase would be found. The temperature, i.e. 300°C, corresponds to the beginning of the final zone for Oil 2 (see Figure 6.2) since it wasn't clear whether to expect the transition phase for Oil 2 in Zone 2 or Zone 3 and observing the residue at 300°C would help clarify this uncertainty.

It was found that the sample taken at 300°C for both oils indeed indicated transition tar-like characteristics. Figure 8.1 shows typical material gathered for both oils.

The sample at this temperature was shiny and sticky, both qualities expected of a tar-like transition material. Furthermore, the sample was a one-piece film stuck to the container. The piece shown in Figure 8.1 had to be broken off and is therefore only a fraction of the entire residue. From the characteristics of the residue, it is clear that the plateau region for Oil 1 does indeed correspond to the transition region, as was hypothesized.

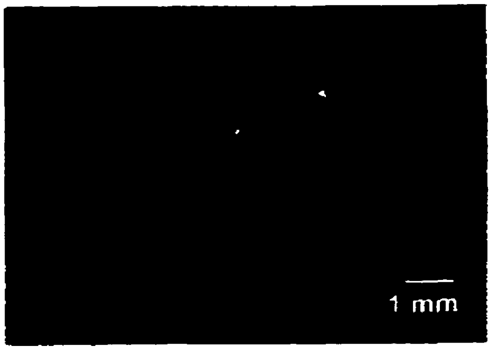


Figure 8.1: Oil 1 & Oil 2 Residue at 300°C

The residue for Oil 2 collected at the same temperature showed similar characteristics as those found for Oil 1. Whereas the residue for Oil 1 was a continuous one-piece film, the residue for Oil 2 had several, smaller films stuck to various corners of the container. Also, there was visibly less total material remaining for Oil 2. This supports the observations made previously concerning the effect of elemental oxygen in the initial material. The presence of oxygen affects the transition of the material to the solid state. For Oil 2, since oxygen is present within the material, the oxidation is not limited to the surface and thus the tar is not found in a single piece but in several smaller pieces. These smaller pieces provide a larger total surface area for oxidation (in addition to the effect of the presence of internal oxygen) which make the weight loss prior to this temperature comparable to that seen in the liquid volatilization part of the process. Thus, no noticeable change in weight loss rate is observed by the balance and no change in the gas-phase products released is observed by the FTIR prior to this temperature.

Since the same characteristics were found for both samples collected at 300°C, it is clear that at this temperature, both oils were in the transition region although it is impossible to clearly determine at what temperature range the transition occurs. For Oil 1, the transition phase most likely occurs in the same temperature region as the plateau in the weight loss curve (i.e., 270-375°C). However, for Oil 2, it is not clear where the transition period begins and where it ends, only that at 300°C, a transition phase exists. Therefore, for the purposes of the solid-phase study of particle evolution, it was evident that a temperature of greater than 300°C would need to be selected as the first temperature of study. (When the sample is in a transition phase, the characteristics of the solid part of the sample cannot be distinguished clearly and thus, the contribution to solid evolution determination is minimum.) The next temperature attempted was 400°C and it was found that the residue was indeed solid (at least, most of the liquid characteristics seen at 300°C were gone and the residue was in several individual pieces).

8.3 Solid Residue Characteristics

The temperatures selected in order to follow the morphological evolution of the solid phase were: 400°C, 650°C and 1000°C. The first temperature was selected because it follows the transition phase and happens close to the temperature where the solid phase first appears. Selecting a temperature of 1000°C was done since the heating process is carried out to this temperature and finally, a temperature between the two was selected to complete the study (i.e. 650°C), which corresponds to the temperature at which the gas-phase portion of the process is seen to be over. The samples were characterized on different levels based on an increasing magnification. First, and most basic, the samples were characterized on a visual level. The samples were also observed under an optical microscope at magnifications of 25 and 40 times. Finally, a closer look at the particle surfaces was achieved via SEM, which was done at magnifications up to 550 times.

8.3.1 Initial Residue Characteristics (400°C):

The solid residue was collected at 400°C and the resulting optical microscope images are shown in Figure 8.2 (a) & (b) for Oils 1 and 2, respectively (at a magnification of 25 times). The two residues exhibited similar characteristics, at least on a visual basis. Both residues were black and showed some characteristics of the transition material, signifying that there most likely remains some organic unburned liquid that was present also in the transition phase particle. The particles are continuous, having a slightly wrinkled surface, are sheet-like and shiny (i.e., similar to the 300°C sample). However, in contrast to the residue found at 300°C, this residue consists of individual particles instead


a. Oil 1 @400°C (x25) b. Oil 2 @400°C (x25)


c. Oil 1 @650°C (x25) d. Oil 2 @650°C (x25)


e. Oil 1 @1000°C (x25) f. Oil 2 @1000°C (x25)


g. Oil 1 @1000°C (x40) h. Oil 2 @1000°C (x40)

Figure 8.2: Optical Microscope Images of Solid Residues

of one sticky film. Furthermore, the particles exhibit a noted decrease in stickiness as compared to the 300°C particles but seem to be more fragile to the touch signifying a loss in some of the liquid properties. Other similarities that are shared between the residues of the two particles are that both residue particles show areas that are thinned out in comparison to the rest of the particle. These areas look like fissures or open gaps in the particle with greater gaps seen for Oil 2 and can be seen in Figures a & b (and can also be seen on the SEM images in Figures 8.3 & 8.4). These fissures are most likely the points where further size reduction occurs by particle break-up since they would result in areas of weakness in the particle structure.

Continuing on a visual comparison, the residues from each oil exhibit some differences. One of the differences is that Oil 2 particles seem to be smaller than Oil 1 particles (400-500 μm compared to ~2 mm for Oil 1). Oil 1 particles seem longer and mostly of the same general size (of the order of millimeters as seen in Figure 8.3). There are also some very small particles which were visible (but not shown) which are in the order of 200 μm across. These particles have similar morphology to the Oil 2 residue seen in Figure 8.4 (i.e. curled at the extremities) yet consist only of a very small fraction of the entire sample. For Oil 1, there is a noted absence of particles of intermediate sizes (i.e., between 200 μm and 1 mm). In the case of Oil 2 particles, however, the largest particles are generally smaller than those for Oil 1 (i.e., in the order of 0.5 mm, as seen in Figure 8.4) and have a more even size distribution (as can be seen in Figure 8.2b, with the presence of particles of many different sizes).

When the particles' characteristics from the two samples were scrutinized more closely by SEM, significantly different morphologies were seen. In general, Oil 1 particles have significantly flatter surfaces than particles for Oil 2 (as is seen in Figure 8.3 for Oil 1, and Figure 8.4 for Oil 2). Oil 1 particles are usually in the order of millimeters, with the selected particle shown in Figure 8.3 being unusually large, about 2 millimeters, but was selected to emphasize the structure typical of these particles. As shown in Figure 8.4, Oil 2 particles are in the order of 0.5 mm in size and exhibit a partially coiled structure, with the onset of curling taking place at the extremities. There is still some areas of relative flatness found in these particles but not as significant as for Oil 1 particles.

Figure 8.3: SEM Micrograph of Oil 1 Particle @ 400°C

Figure 8.4: SEM Micrograph of Oil 2 Particle @ 400°C

8.3.2 Intermediate Residue Characteristics (650°C):

At a temperature of 650°C, both residues seem "fluffy", at least on a visual basis. Images of the residues taken with the optical microscope can be seen in Figure 8.2 c & d for Oil 1 and Oil 2, respectively (at a magnification of 25 times). Compared to the residue at 400°C, the particles now seem to exhibit a greater size distribution in that more intermediate and smaller particles can be found. The particles look similar to wheat in that they are not compact and very loose, especially at the extremities. As can be seen in Figure 8.2 c & d, the particles have very random shapes with the smaller particles clearly resulting from breakage of the larger particles at a weak point in the particle.

However, there are some significant differences between the residues from each oil. The first difference noted was that Oil 1 residue is very light brown in color while Oil 2 residue is a brownish gray, which is not very clear in the images shown (Figure 8.2 c & d) but is quite clear visually. Also, the small particles seen previously for Oil 1 at 400°C are now no longer found. In fact, there is an absence of any particles of similar size for Oil 1 at this temperature. On the other hand, Oil 2 does have small particles as is seen in Figure 8.2 d. When the residues are compared to those at the lower temperature (i.e., Figure 8.2 a & b), it is clear that the size of the particles for Oil 1 remain generally similar with only a slight size reduction whereas the particles for Oil 2 are significantly smaller. In terms of size distribution, Oil 2 still has a wider range of particle sizes whereas Oil 1 particles are generally of similar size and comparatively large.

The particles for Oil 1 are different also in shape than those for Oil 2. Besides being larger, Oil 1 particles seem to be less curled than those for Oil 2 with the Oil 1 surface being relatively continuous and smooth, while the Oil 2 surface is quite "bumpy". A small amount of particles that can be described visually as threadlike are also found in Oil 1 and can be seen in Figure 8.2 c. These types of particles seem tubular and are not seen in the residue for Oil 2. In contrast, the Oil 2 particles consist mainly of particles similar to those seen for Oil 1 but with more severe curling. Oil 2 residue also included the presence of a small amount of white particles (Figure 8.2d) with completely different characteristics. Evidence of particles similar to these white particles was not seen at the lower temperature.

Upon observing the particles by SEM, a better indication of particle sizes was achieved. As can be seen images of typical particles in Figures 8.5 & 8.6, for Oil 1 and Oil 2, respectively, Oil 1 particles were typically in the range of 400-500 μm in size and consisted of generally flat particles with only limited curling at the extremities. The particle shown in Figure 8.6 for Oil 2 represents one of the larger particles, at ~250 μm, with most of the particles present being slightly smaller. Nevertheless, all the particles exhibited the partially coiled structure seen in this Figure.

The visual observation was made that the surface of Oil 1 particles is generally smooth and this is confirmed by the SEM images (see Figure 8.5). The particles for Oil 2 were described above as "bumpy". Figure 8.7 shows a close-up view of the surface of typical Oil 2 particles and it is clear from the image that the surface is covered with bumps, which confirms the observations previously made and shows a significant difference in the solid phase obtained for the two oils.

Finally, the white particles observed in the Oil 2 visual description above were also observed under the SEM. A typical particle is shown in Figure 8.8. Clearly, these particles exhibit completely different morphology and structure than the majority of the particles for this oil sample. These particles have a crystalline structure with a large void space and are typically around 100 μm in size. At this point, it is unclear as to what differences exist between these particles and the typical Oil 2 particles. However, the origin is probably due to the compositional make-up of the respective particles.

8.3.3 <u>Final Residue Characteristics (1000°C)</u>:

At 1000°C, the residues from each oil do not demonstrate much similarities, which is quite a contrast from the samples seen at lower temperatures. Again, there is a difference in residue color and characteristics, as can be seen in Figure 8.2 e & g for Oil 1 and Figure 8.2 f & h for Oil 2 (Figures e & f are at magnification of 25 times, while Figures g & h are at magnification 40 times). Oil 1 residue is dark brown and still shows the same type of structure as was previously seen, i.e., a larger, non-compact, partially curled structure with random shapes. There is also the presence of some (but only very few) smaller, finer particles which cannot be seen in the optical microscope images. However, the particles generated from Oil 2 show completely different characteristics than

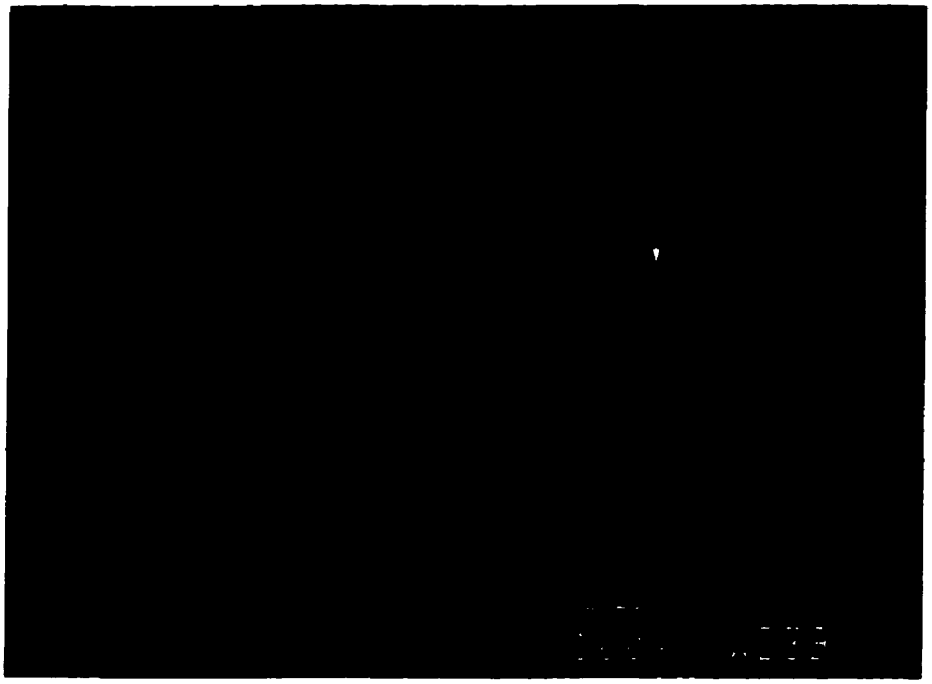


Figure 8.5: SEM Micrograph of Oil 1 Particle @ 650°C

Figure 8.6: SEM Micrograph of Oil 2 Particle @ 650°C

Figure 8.7: SEM Micrograph of Oil 2 Particle Surface @ 650°C

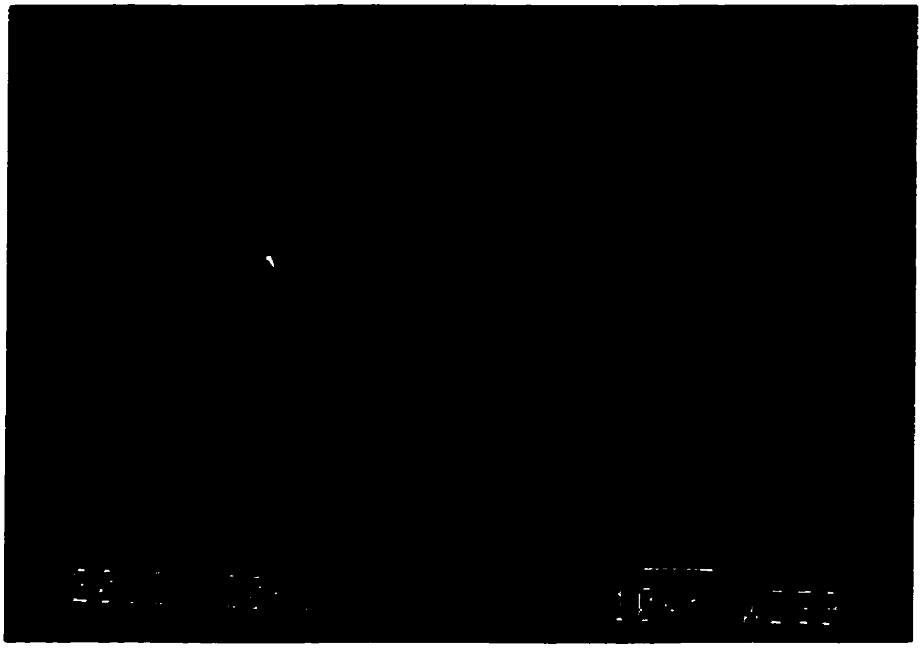


Figure 8.8: SEM Micrograph of Oil 2 Particle @ 650°C

both the Oil 1 residue at the same temperature and the Oil 2 residue previously collected. Oil 2 particles are black and are in the form of a fine powdery material, much like activated charcoal looks like. In addition, the volume of material generated was significantly less than at previous temperatures. The particles seem to be of a much smaller size with a more narrow size distribution (i.e., no larger curled particles similar to those seen at 650°C were found, only small particles). Roughly <10% of the white particles such as those seen at 650°C were also found and can be seen in Figure 8.2f & h.

An SEM image of a typical Oil 1 particle is shown in Figure 8.9. It is clear that the particle still exhibits some form of flatness with a greater degree of curling at the extremities in comparison to the generally flat structure seen at 650°C. The sizes of the particles vary and are generally smaller than the one shown (which is roughly 1.5 mm at its widest) but the particle selected demonstrates clearly the features of the particles generated at this temperature and was selected for that reason. There are also some smaller particles (100 μm) formed in a much less significant amount, which have the morphology seen in Figure 8.10. The particle, since it exhibits some more compact curling, is probably the result of an extremity breaking off a larger particle.

A typical particle generated from Oil 2 is shown in Figures 8.11 & 8.12 and is clearly quite different than either Oil 1 at the same temperature (Figure 8.9) or Oil 2 at a lower temperature. These particles are typically very compact with a smooth surface, signifying that some degree of surface melting has taken place. The particles are mainly the same size, at 100 μm. (Note that although the small particles found for Oil 1 are of the same size, the structure of the particle is completely different: Oil 2 particle is compact, and circular whereas Oil 1 particle is still somewhat compact but curled.)

Finally, another type of particle was also seen by SEM for Oil 2 and shown in Figure 8.13. It is believed that this particle may have evolved from the white particles seen at 650°C since they have a similar structure. These particles are about the same size as the typical particles, i.e., 100 μm. However, they exhibit a much different structure. The particles are more looser and have significant void space, similar to the white particles seen at the lower temperature. Nevertheless, there still seems to be partial melting that was not seen previously which is visible at the bottom of the particle shown in Figure 8.13.

Figure 8.9: SEM Micrograph of Oil 1 Particle @ 1000°C

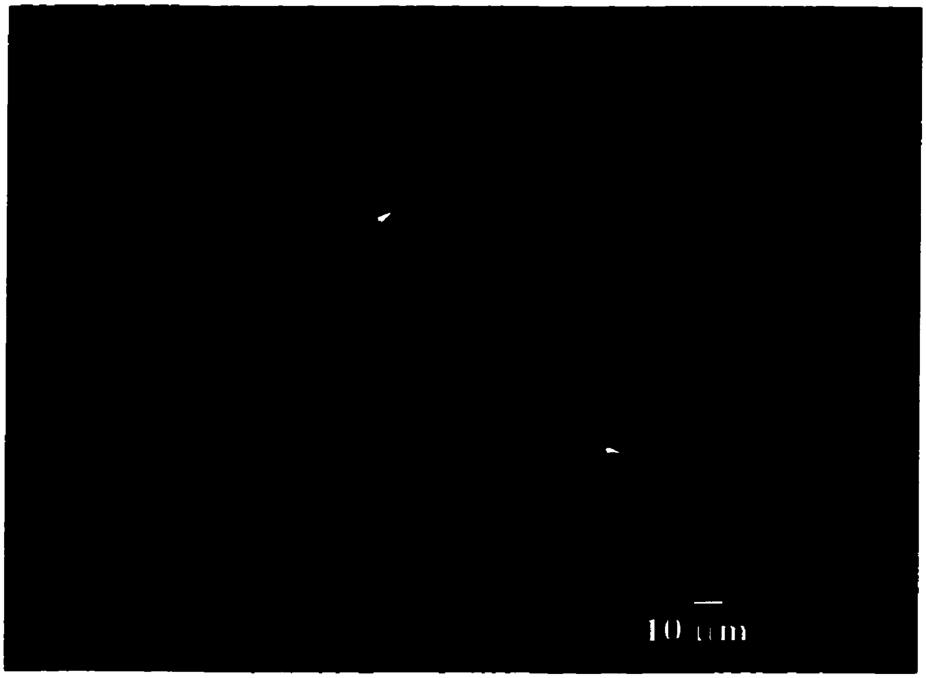


Figure 8.10: SEM Micrograph of Oil 1 Particle @ 1000°C

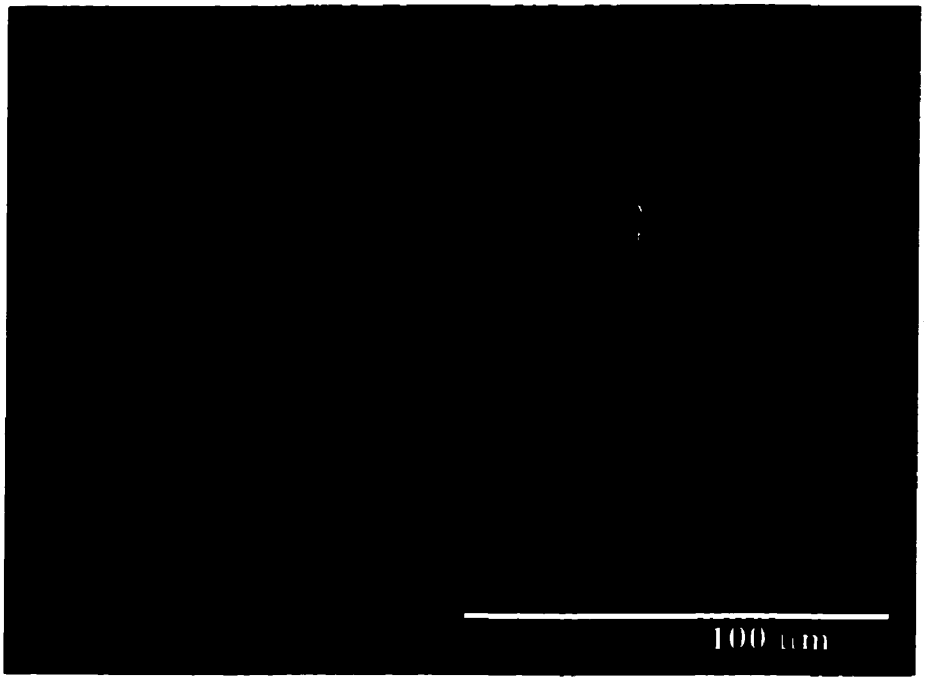


Figure 8.11: SEM Micrograph of Oil 2 Particle @ 1000°C

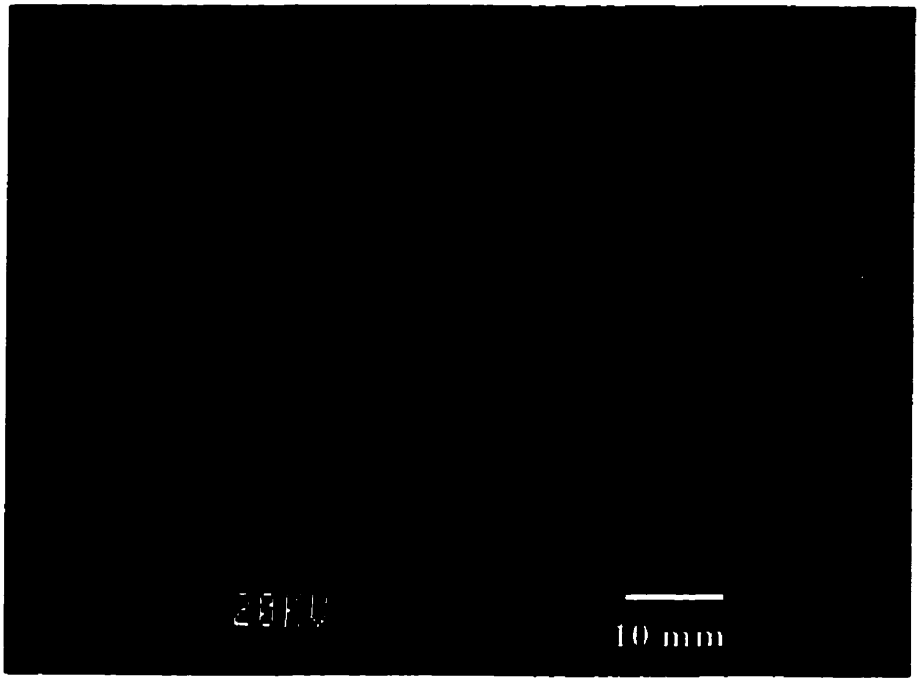


Figure 8.12: SEM Micrograph of Oil 2 Particle @ 1000°C

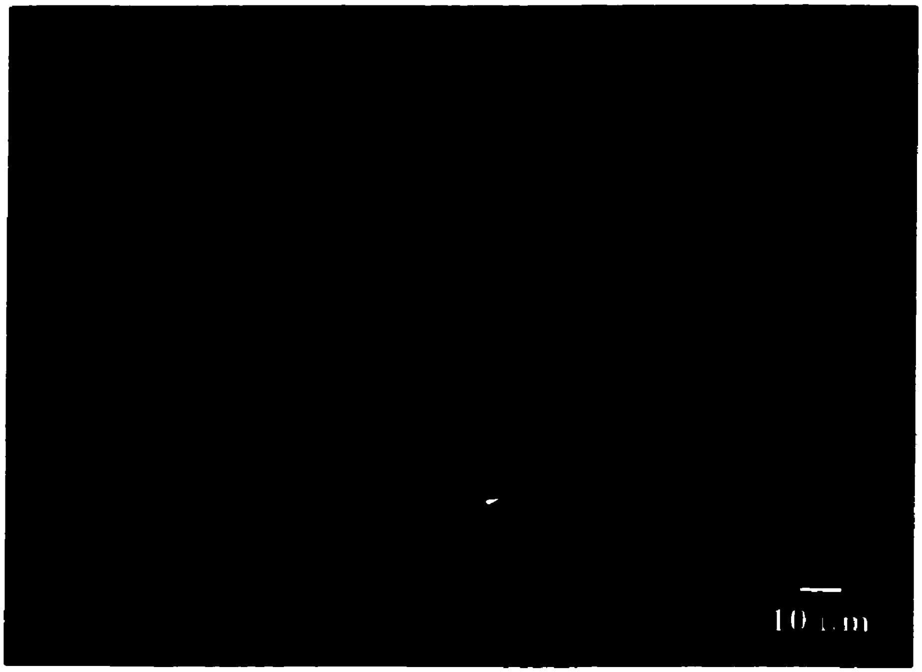


Figure 8.13: SEM Micrograph of Oil 2 Particle @ 1000°C

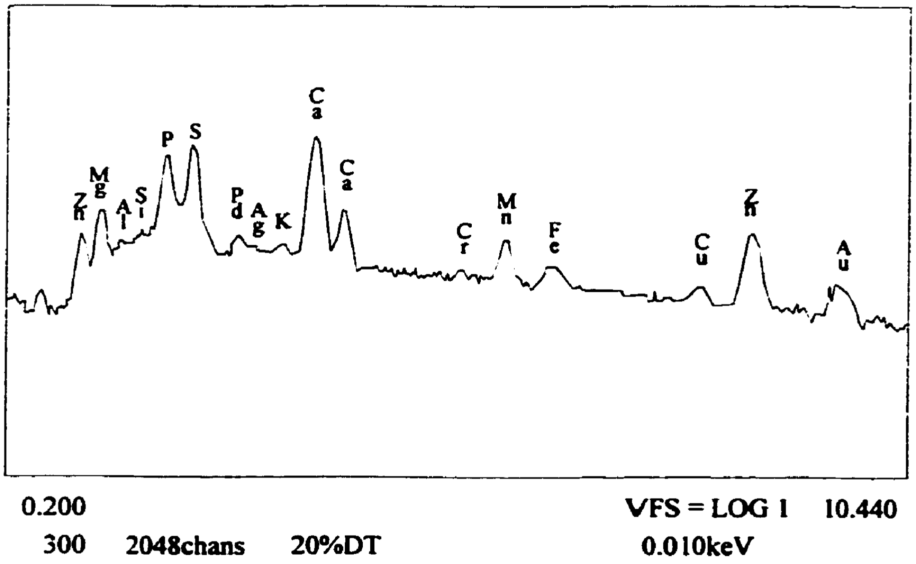


Figure 8.14: Typical EDS Spectrum

8.4 Presence of Metals in Solid Phase

A qualitative study on the presence of metals was done by EDS in order to see what metals were present in the residue. This type of study may allow for determination of metals present and whether there is a relationship of particular metals with temperature. Although the initial metal content in each oil is not known, similar metals were found in both oil residues. Some metals were present at all three temperatures in the residue. These included: zinc, magnesium, phosphorus, calcium, manganese, iron, silver, sodium, potassium and copper. Other metals present showed some patterns of interest. A typical EDS spectrum is shown in Figure 8.14.

Neither residue showed any chromium content at 400°C. However, at 650°C, there was still no Cr in Oil 2 residue, but Cr was seen on the surface of the Oil 1 residue. Finally, at 1000°C, Cr was present in both residues. It seems that as the temperature increases, the Cr migrates to the surface layers of the particles. Another possible explanation could be that, by the higher temperatures, as the particle size gets smaller, perhaps the Cr becomes concentrated enough to be detected.

In terms of sulfur content, the EDS study showed that both residues showed sulfur for samples at both 400°C and 650°C. However, at 1000°C, Oil 1 still had S while Oil 2 did not. This is consistent with the initial S present, which is 0.54 wt % for Oil 1 and 0.35 wt % for Oil 2. Since Oil 2 has about half the sulfur of Oil 1, it is expected that Oil 2 would lose its sulfur first. The S in the solid, in this part of the process, would be oxidized and SO_2 (90%) and SO_3 (10%) are expected to be formed.

There was no Ni detected by EDS at temperatures of 400°C and 650°C for either oil. However, at 1000°C, there was still no Ni detected in Oil 1 residue but was in Oil 2. Finally, in terms of Cl content detected by EDS, Oil 2 never showed any (which is to be expected since Oil 2 initially has only 0.0091 wt % Cl). However, this is not the case for Oil 1 which has initially 1.12 wt % Cl. Therefore, at 400°C, Oil 1 residue showed Cl and did not for the higher temperatures. This suggests that the chlorine present in Oil 1 is lost at some temperature between 400°C and the next temperature measurement, 650°C. The presence of Cl is important in terms of toxic metal behavior since it is known that the chloride species of a given metal is much more volatile than in other forms.[28]

Chapter 9: Process Mechanism

Various aspects of the used oil slow heating process have been studied in this work (i.e., weight behavior, gas phase evolution of both CO_2 and hydrocarbons and evolution of solid residues for two different used lubricating motor oils). Based on all observations made, it is possible to propose a plausible mechanism for the transformation of the oil samples in an oxidative environment, when heated at 3°C/min from 30°C to 650°C, followed by a 5°C/min heating rate from 650°C to a final temperature of 1000°C.

9.1 Overall Process Mechanism

First, an overall mechanism is proposed that applies to both oils in which the dominant features are described. A schematic of the overall transformation mechanism for a spent lubricating oil is shown in Figure 9.1. It is believed that, under the conditions studied, the lubricating oil undergoes changes as is shown in the figure. The transformation process is divided into four stages similar to the zones assigned in the weight loss curve for Oil 1 (Figure 6.1). In each stage, different processes dominate and these dominating features are used as a basis for stage designation. Although the major features in each stage are shown in Figure 9.1, the processes the oils undergo are gradual due to the slow heating rate. Thus, the designations are not clearly distinct from one another and therefore, some overlap occurs. (Similar separation of a crude oil combustion-like process was obtained from a kinetic point of view in other studies.[9,14,29])

The transformation begins in Stage 1, called "Initial Volatilization", where the sample is entirely liquid as the heating process begins (this is represented schematically on the upper left portion of Figure 9.1). Since the heating process is slow, and the material temperature is still low (i.e., less than about 150°C) there is an initial period where very little occurs in terms of sample transformation. There is material escaping in this region as is evidenced by the small amount of weight loss detected by the balance over the first part of the process (see Figures 6.1 and 6.2). However, the amounts released are insignificant in comparison to the rest of the process. Also, no major gas-phase products were detected with the FTIR during the Initial Volatilization since the small amount of material

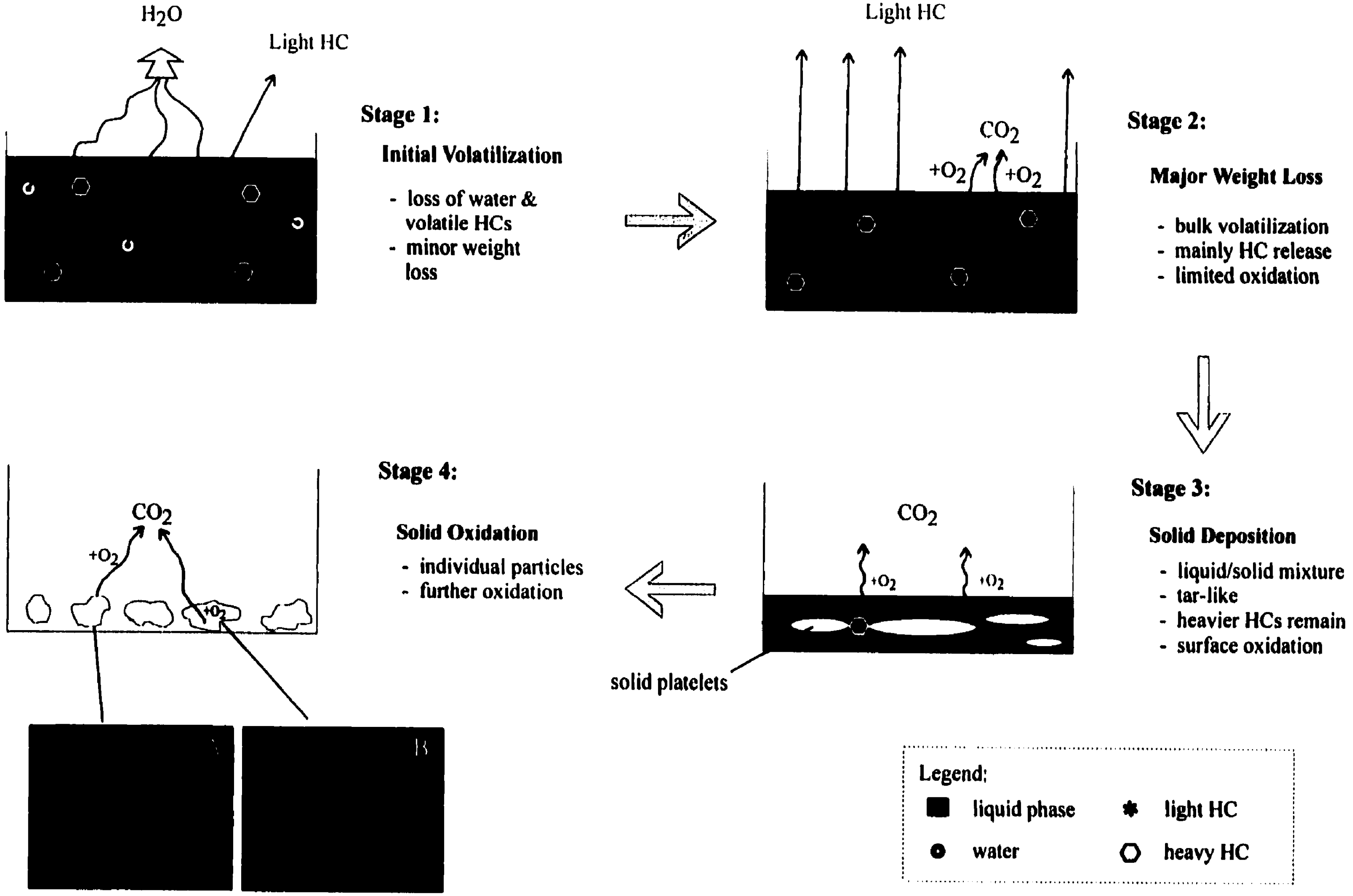


Figure 9.1: Overall Oil Transformation Mechanism

that is released is done so over a significant time period (about 30 minutes) and thus, the concentration of the released material would be low. Due to the sample makeup, this material probably consists of very light hydrocarbons as well as any H_2O present in the oil (in this case, <0.1 wt% & 0.3 wt% of water was present for Oil 1 and Oil 2, respectively). This is represented in the figure by the vaporization of water particles with a limited amount of light hydrocarbon vaporization.

After this initial stage, the most significant weight loss in the process occurs for both oils and thus, this part of the process is referred to as the "Major Weight Loss" Stage (labeled as Stage 2 on the upper right of Figure 9.1). This weight loss is believed to correspond to the bulk volatilization of the light liquid hydrocarbons present in the oil (as seen in the gas evolution profiles and illustrated in the figure). Since the temperature is still relatively low (i.e. ~250°C), no significant oxidation occurs. However, a limited amount of oxidation does indeed occur in this part of the process as is indicated by the presence of CO_2 (see Figure 7.2 for temperature resolved CO_2 profiles). This signifies that a small portion of the volatilized hydrocarbons react with the oxygen in the air as they are released. This is shown in the figure via the majority of the process being straight vaporization of the light hydrocarbons present in the sample and only a limited amount of oxidation of those same light hydrocarbons. In similar studies using crude oil, the low temperature oxidation equivalent to the Major Weight Loss Stage was attributed to reactions generating oxygenated hydrocarbons.[9] There was evidence of such compounds in the FTIR spectra collected (see Figure 4.4 peak at 1700 cm^{-1} which could represent a C=O functional group) so this is a possible, yet unconfirmed, reaction taking place in this stage. However, since a lubricating oil contains lighter fractions than a crude oil, it is expected that more volatilization occurs than for crude oil. Other studies have confirmed that in addition to oxygenation occurring, evaporation and distillation of hydrocarbons also occur in this part of the process.[29]

As vaporization proceeds, the sample will reach a point where most of the lighter hydrocarbons have volatilized, depositing a liquid/solid transition material, herein referred to as "tar". This material, most likely including some form of solid platelets, thus contains some of the heavier hydrocarbons initially found in the oil sample. This part of the process, called the "Solid Deposition Stage" and seen in Figure 9.1 as Stage 3, was shown to correspond to the plateau region seen in the weight loss curve for Oil 1 (Figure 6.1) at approximately 300°C. The Solid Deposition Stage is believed to be dominated by a surface process, explaining the slow down in the weight loss seen for Oil 1. As was shown by the image of both samples at 300°C (Figure 8.1), the material is a film-like structure that is partially liquid. Therefore, whatever oxidation takes place in this stage, it is limited to the top surface layers of the residue, as is demonstrated in Figure 9.1 by the oxidation arrows emanating only from the sample surface. Some hydrocarbons are trapped below these layers without being able to volatilize until the layers above them have reacted. This is in contrast to the processes occurring in the previous stage, i.e. the Major Weight Loss Stage, where volatilization is not limited to the surface but occurs throughout the entire sample which is liquid and does not hinder the vaporization of the hydrocarbons. (For the crude oil process, a similar region was attributed to distillation and pyrolysis processes leading to solid fuel deposition.[9])

During the Solid Deposition Stage, there is a marked difference in the two oils in terms of the behaviors observed, despite the dominant features described above being similar. Oil 1 shows a drastic slow down in the weight loss during this part of the process while none is visible for Oil 2. It was shown via the optical microscope images taken (refer to Figure 8.1) that this region is accounted for by the transition of the sample from its liquid state to the solid state. Although it was seen that both oils undergo this transition in the same general temperature region, the weight loss and the gas-phase evolution only show evidence of this transformation for Oil 1 and not for Oil 2. Since Oil 1 does not have elemental oxygen within it to aid the oxidation process, it is believed that the rate of formation of this tar and its subsequent oxidation are limited by the mass transfer of oxygen from the reaction air to the surface of the liquid-solid sample and this explains the slow-down in the process for Oil 1. Whereas for Oil 2, the oxygen present aids the oxidation process by having oxidation reactions take place internally, speeding up the process of tar formation and subsequent breakup of the film that is formed.

The tar material for Oil 1 is in the form of a one-piece non-porous film with only a limited amount of surface exposed to reaction air. Because of this limitation in the reaction process, the duration and rate of the transition part of the process will depend on the amount of material in the container at the time the Solid Deposition Stage is occurring. This is true since only the surface of the material will react and therefore, material that could otherwise be oxidized would be trapped beneath the top layer of non-porous tar that is formed until the surface layers are oxidized. This behavior explains the dependence on initial sample weight for Oil 1 that was shown in Figure 4.9. The more material used initially, the more material will remain when the transition tar layer first forms, thus trapping hydrocarbons that would otherwise be oxidized until a path is formed for access to the reacting medium.

For Oil 2, the tar is in several film-like pieces during the Solid Deposition Stage (compared to one for Oil 1). The presence of several film-like pieces increases the surface area of the sample that is exposed to oxidation and vaporization of hydrocarbons. Also, there may still remain some internal oxygen in Oil 2 at this point in the process which would further increase the rapidity of the process. Therefore, for Oil 2, although this liquid/solid transition occurs in the same general temperature range as for Oil 1 and has the same processes occurring (i.e. mainly surface oxidation), the slow-down is not noticeable. Oil 2 differs from Oil 1 in initial elemental oxygen content which probably explains this difference. (Oil 1 initially had <0.5 wt% while Oil 2 had 2.4 wt% elemental oxygen.) The oxygen causes some internal oxidation to take place, thus affecting the initial formation of the tar material. This explains the formation of distinct tar film pieces for Oil 2, which facilitates further oxidation as temperature increases by increasing surface area with, perhaps, further internal oxidation taking place.

Also, as was seen in the SEM images of Oil 2 solid particles (see Figure 8.4), the internal oxygen increases the formation of pores near the surface which further increase access of the reaction air to the residue interior. In other words, while for Oil 1, oxidation is limited at all times to the surface of the sample, the oxygen present in Oil 2 allows for at least partial oxidation from within the sample and increased surface area for reaction air to access the interior of the film. This results in a smoother transition from liquid to solid in Oil 2 and accounts for the lack of a plateau region for this sample in the weight curve.

Following the Solid Deposition Stage, the tar material becomes more solid and eventually breaks up into individual particles for both oil samples (as is shown in Figure 9.1, labeled as Stage 4: Solid Oxidation). These particles still contain some hydrocarbons which will continue to oxidize as heating progresses, thus explaining the final weight loss seen in both cases in the Solid Oxidation Stage. Since these hydrocarbons are associated with solid particles and are most likely higher boiling point hydrocarbons, direct vaporization of the hydrocarbons is not seen but instead, this zone is characterized by mainly oxidation and thus, the presence of CO_2 (see Figure 7.2 for gas-phase evolution profiles). That is, the hydrocarbon release is slow enough and the temperature is high enough (approximately 450°C) so as to allow for oxidation to take place within the high temperature region of the furnace. (Oxygenated hydrocarbons were attributed to the solid phase oxidation in the similar crude oil process which generated only CO_2, CO and H_2O.[9]) However, there are differences in the characteristics of the particles found for each oil due mainly to the formation processes in the Solid Deposition Stage. Thus, in Figure 9.1, in conjunction to the general oxidation process illustrated, SEM images of typical particles initially formed are included to show these differences for Oil 1 (Image A) and Oil 2 (Image B). Oil 1 initial particles are generally flat and large, while Oil 2 particles are smaller and partially coiled.

Thus, the final Solid Oxidation Stage in both cases is the result of the particles that are generated from the Solid Deposition Stage material as they are being further oxidized. Since the Solid Deposition Stage is affected by the sample internal oxygen content, the particles formed for each oil have different characteristics. The reason for the greater weight loss in this stage for Oil 1 is that, following the transition stage which is limited to a surface oxidation, the solid particles produced still have significant amounts of hydrocarbons trapped within the particles that were unable to oxidize earlier. As the temperature increases and the surface layer erodes, a breakthrough occurs and these hydrocarbons escape and oxidize (as seen in Figure 7.2 showing CO_2 profiles), accounting for the greater weight loss compared to Oil 2 where the same heavy hydrocarbons can oxidize earlier in the heating process because the surface area exposure to the air is greater.

9.2 Mechanism of Solid Particle Evolution

The processes that lead up to the Solid Oxidation Stage have slight differences due mainly to the initial oxygen content of the starting material as discussed above. Because of this, the initial solid particles generated have different characteristics as shown in Images A&B in Figure 9.1. Due to the initial particles having different characteristics, the evolution of these particles as they get heated to a final temperature of 1000°C is also different for each oil and the processes that dominate each oil's Solid Oxidation Stage are different (this is illustrated in Figure 9.1 by the arrows pointing to a particle surface and a particle interior). Therefore, through the observations made from visual, optical microscope and SEM studies, the differences in the solid evolution between the two oils is explained in terms of a solid particle mechanism for each oil. A detailed schematic of the solid particle evolution mechanism proposed is shown in Figure 9.2. The evolution from a temperature of 400°C (approximately where individual solid particles can first be identified) on the left-most part of the figure to a final temperature of 1000°C to the far right is shown in the figure. The upper part of the figure shows the evolution for the Oil 1 solid particles while the lower part shows the same for Oil 2. Typical SEM micrographs (previously shown in Chapter 8, Figures 8.3, 8.9, 8.4 & 8.12) representing the particle evolution are also included in Figure 9.2.

It was very evident based on initial visual observations that, at the end of the process, the solid particles generated by each oil were significantly different. Although the initial particles for each oil have clearly different characteristics, the level of difference in the final particles clearly suggested that the evolution of the solid particles during the heating period following their formation contained some different mechanisms as well.

9.2.1 Oil 1 Solid Particle Evolution:

The Oil 1 solid phase evolution is shown at the top of Figure 9.2. At the onset of individual particle formation, Oil 1 particles are generally large (typically 1.5-2.0 mm), flat sheet-like particles with a smooth surface structure, as is seen in the figure in the SEM micrograph representing the initial Oil 1 particle. By the end of the heating process, these particles evolve to partially coiled particles being still relatively large, at 0.8-1.4 mm, seen at the top right of the figure, in terms of schematic and SEM representations. (Along the

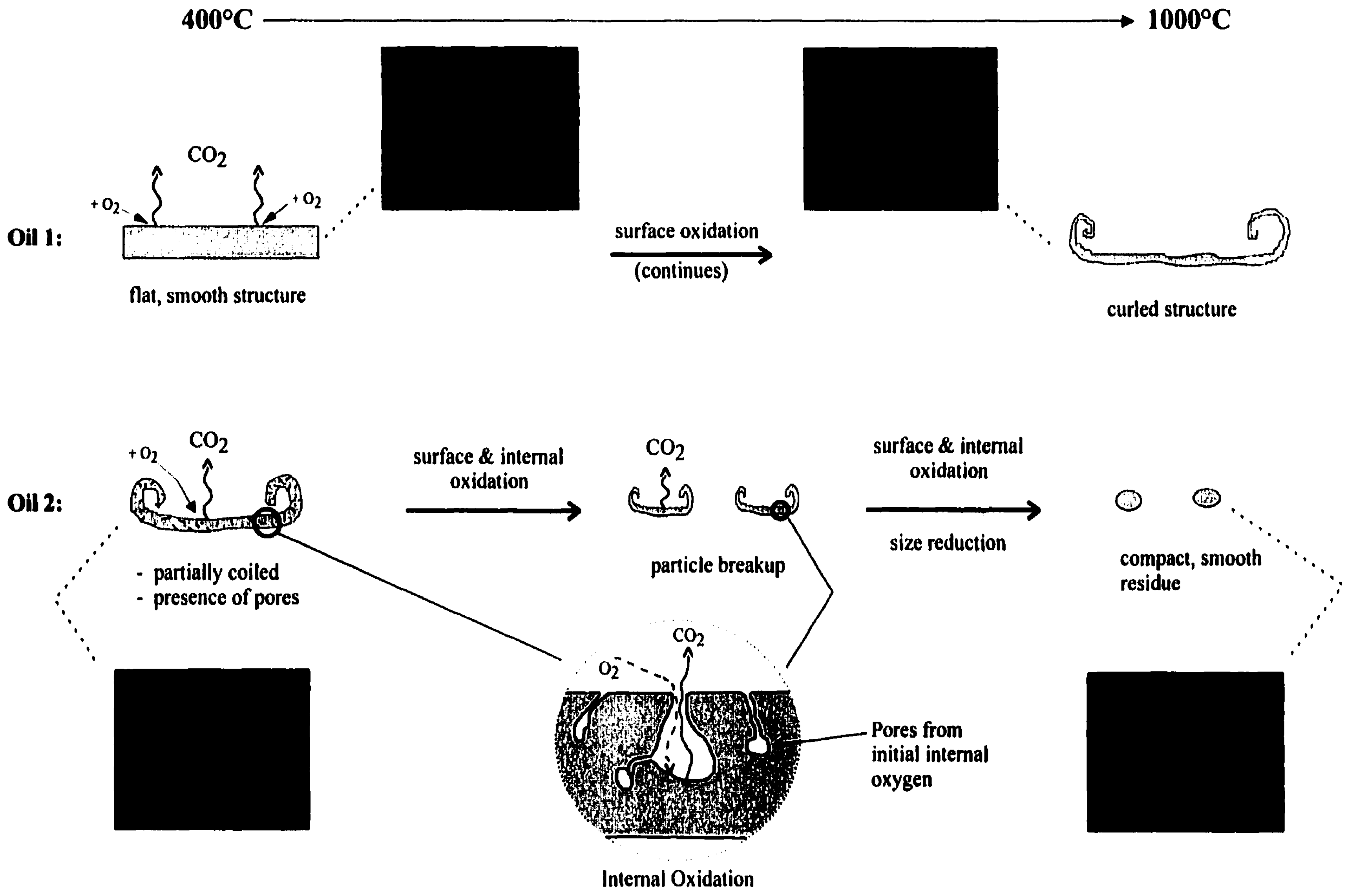


Figure 9.2: Solid Particle Evolution

process, small parts of the particle break off and it is hypothesized that this is where fly ash comes from, if the particles are sufficiently small.) The behavior of Oil 1 particles in conjunction with the weight and gas-phase observations lead to the conclusion that the process taking place in this part of the transformation is limited to surface oxidation alone. That is, that the carbonaceous material present in the particles react solely at the reaction gas-solid interface of the sample. This would explain why a second ignition temperature was not seen in Figure 6.5.

At 400°C, the residue for Oil 1 still has some carbonaceous material and is, therefore, "wetter". The sample at this point, maintains over 20% of its mass, as was seen in Figure 6.1. As heating proceeds, portions of the sheet lose some material to oxidation (and some volatilization) at the surface; i.e. the sample "dries", which causes the particle to curl partially in the areas of local mass loss. Certain areas will not be strong enough to maintain contact with the larger piece and will break off (i.e., the stresses caused from the curling tendency of the particle may, at some point, become too great). These types of particles were seen in the sample as well (i.e. smaller, shriveled up pieces as seen in Figure 8.10). As the temperature rises, the surface layers continue to lose carbonaceous material and volatile matter (i.e. they dry). The drying takes place at different rates along the particle depending on the distribution of the remaining hydrocarbons, causing differential stresses in the particle surface and thus, the top of the particle shrinks and shrivels, causing a curling nature at the extremities of the final particle as is shown in Figure 9.2 for Oil 1 at 1000°C.

Just based on this level of observation, a conclusion cannot be made as to whether these particles would be conducive to leaching. It is hypothesized that due to the nature of the particles, leaching would be easy. However, it is also believed that the particles would be more shriveled if the heating rate in the Solid Oxidation Stage were increased and thus, if this is proven to be correct, the more compact, shriveled particles could ultimately be dense enough to prevent or minimize leaching. In other words, if particle characteristics could be controlled by some of the process parameters, a more environmentally friendly solid residue could be generated. Since for oils, the major portion of the burning process is over early in the process, the temperature history from this point onwards could play an important role in the solid residue part of the process.

9.2.2 Oil 2 Solid Particle Evolution:

Evolution of solid particles formed during Oil 2 heating is shown on the lower half of Figure 9.2. For Oil 2, the evolution is clearly different than for Oil 1. At 400°C (at the bottom left of the figure), the particle for Oil 2 has a partially coiled structure with the presence of surface pores, as is seen by the SEM insert. By the final temperature of 1000°C (at the bottom right of the figure), the particles have a much more compact structure with a continuous surface. Also, the size of the particles are significantly smaller. At 400°C, the particles are ~0.6 mm and by 1000°C, the particle has significantly reduced size to ~0.2 mm. From a leaching point of view, the compact structure of the final ash should deter leaching of hazardous metals from taking place. Therefore, this type of structure would be advantageous over the flatter, less compact structure that Oil 1 generates.

The surface oxidation process described for Oil 1 also takes place for Oil 2 particles as is demonstrated in the figure (i.e. hydrocarbons at the particle surface oxidize when they come into contact with oxygen). However, due to the pores formed in these particles during the Solid Deposition Stage (which are due to initial oxygen content) further oxidation occurs internally. The reaction gas (air) can access the interior of the particle as well as the surface and thus the effective surface area exposed to oxidation conditions increases, explaining why a second ignition event was found in Figure 6.6 for Oil 2. The combination of the two processes means that, as the particles continue to curl up due to the surface oxidation process, they tend to break up more readily because of the internal oxidation occurring. As these processes continue during the heating, the final particles become very small, compact and smooth.

9.2.3 Summary:

The differences in particle evolution for the two samples are summarized as follows. From what is seen by the SEM images, the Oil 1 solid phase oxidation process is predominantly one of surface oxidation. The particle generally starts off flat and oxidizes on the surface only. This causes the particle to shrink on the surface while the lower portion remains intact, causing the particle extremities to curl up and the general size of the particle to remain the same (i.e. not much particle break-up occurs). Since Oil 1 contains no elemental oxygen initially, this can explain why the initial solid particle formed is flat, without pores that would promote internal oxidation.

Oil 2 shows a different particle morphology initially. The initial particle (at 400°C) is already partially coiled and smaller than Oil 1 particles at the same temperature. This is caused by the elemental oxygen present in Oil 2, increasing the amount of internal oxidation during the Solid Deposition Stage and subsequent formation of the particle is faster. While the particle heats up and continues to oxidize, in addition to surface oxidation, the pores formed during the transition stage allow for oxygen to penetrate the particle, thus allowing internal oxidation to also take place. This results in the particle not only curling up from surface oxidation but also breaking up due to the internal oxidation. As the temperature reaches 1000°C, the final particle is therefore, smaller and more compact due to the two processes taking place simultaneously.

Chapter 10: Polycyclic Aromatic Hydrocarbon (PAH) Behavior

10.1 Introduction

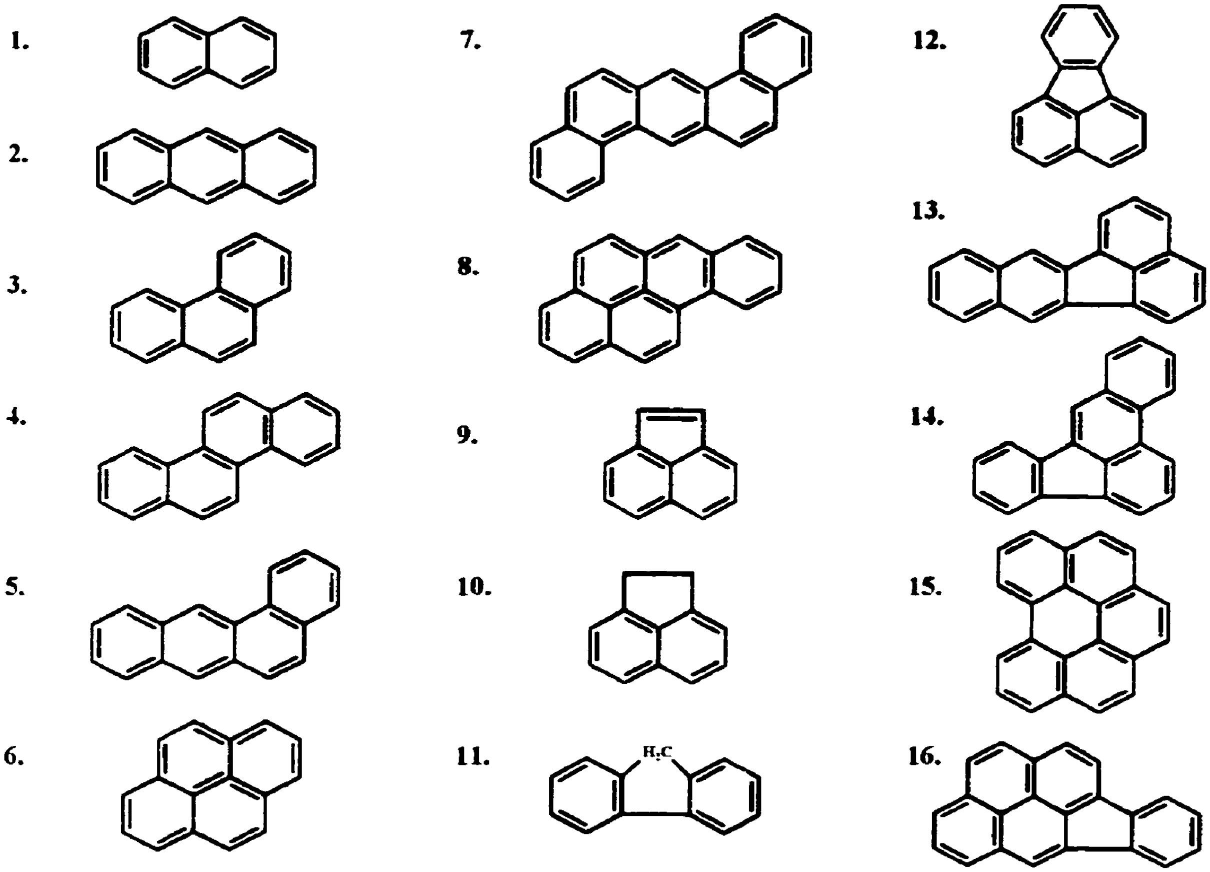
With the current knowledge on the behavior of the two used oils during the slow heating process, it is important to address some of the environmental concerns associated with the process. One of the more important areas of environmental concerns found in most combustion processes, especially those involving hydrocarbons, is the release of hazardous compounds such as Polycyclic Aromatic Hydrocarbons, PAHs. Therefore, some initial attempts at studying the release of PAHs during the process were made.

10.1.1 Physical and Chemical Properties of PAHs:

Polycyclic Aromatic Hydrocarbons (PAHs) are compounds that contain only carbon and hydrogen atoms, found in two or more fused benzene rings of various arrangements. Generally, these compounds have low vapor pressures and thus, have a tendency to be found in a condensed phase.[30] These compounds, including substituted molecules, are of interest because many of them have been found to be carcinogenic and mutagenic.[31,32] The Environmental Protection Agency (EPA) in the United States has qualified 16 PAHs as priority pollutants[33] (i.e. pollutants that warrant regulation). Figure 10.1 shows these compounds and those that are marked with an asterisk(*) are suspected or known carcinogens. Table 10.1 gives selected physical properties of these same PAHs.

PAHs are common products of incomplete combustion of hydrocarbons and are produced in a variety of anthropogenic and natural systems. During incomplete combustion processes (or high temperature pyrolytic processes), unburned hydrocarbons are released, of which PAHs are a part of. Since many PAHs have high boiling points (as demonstrated in Table 10.1), they have always been associated with soot, fly ash, and other particulates formed during the combustion process, mainly in the respirable size range of less than about 3 μm diameter[34]. However, this does not exclude vapor phase PAHs from being present in the atmosphere. Recently, with the advent of better analytical technology, it was found that PAHs are indeed being released in the gas phase during these processes. Therefore, it is no longer adequate, environmentally, to capture all solid particles to prevent PAH release. There also needs to be a way to reduce the gas phase

Figure 10.1: Structures of PAHs as EPA priority pollutants[33]



1=naphthalene, 2=anthracene, 3=phenanthrene, 4=chrysene, 5=benz[*a*]anthracene*, 6=pyrene, 7=dibenz[*a,h*]anthracene*, 8=benzo[*a*]pyrene*, 9=acenaphthylene, 10=acenaphtene, 11=fluorene, 12=fluoranthene, 13=benzo[*k*]fluoranthene*, 14=benzo[*b*]fluoranthene*, 15=benzo[*ghi*]perylene*, 16=indeno[1,2,3-*cd*]pyrene*.

Table 10.1: Priority Pollutant PAH Properties [35]

Compound	Formula	MW	Melting Pt, °C	Boiling Pt., °C
naphthalene	$C_{10}H_8$	128.19	81	218
anthracene	$C_{14}H_{10}$	178.24	216	340
phenanthrene	$C_{14}H_{10}$	178.24	101	338
chrysene	$C_{18}H_{12}$	228.30	256	441
benz(a)anthracene	$C_{18}H_{12}$	228.30	162	435
pyrene	$C_{16}H_{10}$	202.26	156	393
dibenz(a,h)anthracene	$C_{22}H_{14}$	278.36	205	---
benzo(a)pyrene	$C_{20}H_{12}$	252.32	177	496
acenaphthylene	$C_{12}H_8$	152.21	93	270
acenaphthene	$C_{12}H_{10}$	154.21	96	279
fluorene	$C_{13}H_{10}$	166.23	117	294
fluoranthene	$C_{16}H_{10}$	202.26	111	383
benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	217	481
benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	168	481
benzo(ghi)perylene	$C_{22}H_{12}$	276.34	278	---
indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	---	---

PAH emissions to make combustion processes more environmentally credible, as well as limiting exposure to PAHs and therefore, decreasing health risk.

The factors that determine whether PAHs generated are found in the vapor or the condensed phase are: 1) the vapor pressure of the PAH (which is a function of temperature); 2) the process temperature; 3) PAH concentration; 4) the amount of fine particles generated (in terms of surface area for adsorption of the PAH); and 5) affinity of individual PAHs for the particles' organic matrix.[36] In general, the more surface area there is in terms of particles, the greater the possibility of PAH adsorption and condensation. Also, PAHs with a molecular weight less than that of pyrene (MW=202) are found, to a large extent, in the gas phase.[36]

10.1.2 Health Concerns:

Why the interest in PAHs? Some of these compounds are carcinogenic and mutagenic and it is therefore, in the public interest to understand their behavior in processes such as the one being studied, to eventually be able to minimize human exposure to these compounds. Some PAHs, particularly those with four or five aromatic rings (such as benzo(a)pyrene), are known to cause mutations in human cells and cancer in rodents, and so, PAHs are among the compounds regulated as hazardous air pollutants under the United States Clean Air Act.[31] In Canada, PAHs are not yet regulated. (Note that PAHs are partly responsible for the carcinogenicity of cigarette smoke!)[37]

PAHs were among the first atmospheric pollutants to be identified as being carcinogenic.[36] As far back as 1775, a British surgeon named Sir Percival Pott observed an increase in cancer in chimney sweeps. He hypothesized that the soot and tar that they were exposed to was the cause of the cancer. It wasn't until 1915, that researchers, by being able to induce tumors with coal tar, first established the link that Pott had observed. (This was achieved by painting the inside of rabbit ears until tumors developed.)[38,39,40] Eventually, it was discovered that the carcinogenic components that these and other similar compounds consisted were PAHs. By 1976, over 30 PAHs and several hundred derivatives of PAHs were reported to have some degree of carcinogenic effect.[38, 39, 40]

Despite the fact that PAHs are produced only in trace amounts in most combustion processes, the cumulative amounts from all the combustion sources may be considerable.[31]

There is concern that continuous low-level exposure to PAHs could increase the risk of cancer and genetic defects, although the level of this risk is yet to be established. Thus, it is important to limit the release of these compounds from combustion processes.

10.1.3 Sources of PAHs:

PAHs can be formed by anthropogenic as well as natural processes, with the greatest amount coming from man-made sources.[36] The natural sources of PAH are mainly from forest fires, biosynthesis processes, and volcanic eruptions, but will not be discussed here, so as to concentrate strictly on anthropogenic sources which are much more important to air pollution.[38]

PAHs are, however, mainly emitted by anthropogenic sources, namely by the combustion of organic fuels, such as used oils. In these processes, PAHs are formed mainly in two ways: 1) pyrolysis or incomplete combustion; & 2) carbonization processes (i.e. carbon growth).[38] PAH release is not limited to combustion processes (e.g., evaporation of gasoline containing PAHs) but this is the major anthropogenic contributor and of most direct interest to the area of study since some to what is learned in this research on used oils may be applicable to other types of combustion processes, especially if used oil is used as a supplemental fuel.

Anthropogenic sources can be divided into two classes: mobile sources and stationary sources. Mobile sources of PAHs include diesel and gasoline operated vehicles, while stationary sources include a wide variety of combustion processes, such as residential heating, power generation and industrial activities (which are possible consumers of used oil as a fuel). Table 10.2 shows different sources of stationary and mobile PAHs. Evidently, stationary sources tend to result in localized high concentrations of PAHs while mobile sources spread the PAH release over a wider region. The highest concentrations of PAH found in the atmosphere are, logically, located near the emission sources (i.e. urban and industrial regions). However, due to atmospheric transport phenomena, PAHs have been found even in the most pristine, remote areas of the world and thus, PAH release takes on a global concern.

Although PAHs have been investigated and quantified by many different researchers for different combustion processes, there is as yet no standard method for

Table 10.2: Sources of PAH[38]

Stationary sources

1. Residential heating
   - Furnaces, fireplaces, and stoves (wood and coal)
   - Gas burners
2. Industry
   - Coke production
   - Carbon black production
   - Petroleum catalytic cracking
   - Asphalt production
   - Aluminum smelting
   - Iron and steel sintering
   - Ferroalloy industry
3. Power and heat generation
   - Coal-and oil-fired power plants
   - Wood- and peat-fired power plants
   - Industrial and commercial boilers
4. Incineration and open fires
   - Municipal and industrial incinerators
   - Refuse burning
   - Forest fires
   - Structural fires
   - Agricultural burning

Mobile sources

5. Gasoline-engine automobiles
   - Diesel-engine automobiles
   - Rubber tire wear
   - Airplanes
   - Sea traffic

studying PAHs and thus, each researcher provides different types of data (i.e. different collection and quantification methods and different PAHs). This has the implication of making comparisons of different combustion processes difficult. Nevertheless comparison of PAH emissions of different combustion sources is quite interesting as an order of magnitude indication of the efficiency of different processes and fuels. A number of Tables follow that show some interesting comparisons, (despite being taken from different researchers, different experimental conditions, etc.).

Table 10.3 shows estimates of PAH emission in Norway, Sweden and the USA in M.T/yr. Since PAHs are not yet regulated in Canada, similar data is not available. It is interesting to note that stationary sources account for the majority of PAHs emitted. Despite the lower percentage from mobile sources, these tend to be highly concentrated within certain areas (i.e. urban centers) and therefore, are cause for local episodes of high levels of PAH. A significant amount of PAHs are emitted in industrial processes such as aluminum production in Norway and the U.S., while Sweden produces a significant amount through residential combustion processes. Also from Table 10.3, the U.S. is

Table 10.3: Estimated PAH Emission[38]

	Norway		Sweden		U.S.A.	
Source	**M.T./yr**	**%**	**M.T./yr**	**%**	**M.T./yr**	**%**
Residential combustion						
Wood, coal	48	16	96	38	700	12
Oil, gas	14.5	5	36	14	15	0.3
Industrial production						
Coke manufacturing	5.1	2	18	7	630	11
Carbon black	—	—	<0.1	<0.1	3	<0.1
Asphalt production	0.1	<0.1	0.3	<0.1	4	<0.1
Aluminum production	160	54	35	14	1000	17
Iron and steel works	34	12	—	—	—	—
Ferroalloy industry	3.5	1	1	0.4	—	—
Petroleum cracking	—	—	<0.1	<0.1	—	—
Power generation						
Coal and oil-fired power plants	—	—	<0.1	<0.1	1	<0.1
Peat, wood, straw	0.1	<0.1	6.5	3	—	—
Industrial boilers	1.2	0.4	6.5	3	400	7
Incineration						
Municipal incineration	0.3	<0.1	2.2	0.9	50	0.8
Open burning	0.4	<0.1	—	—	100	2
Forest fires	7	2	1.3	0.5	1000	17
Agricultural burning	6	2	—	—	—	—
Mobile sources						
Gasoline automobiles	13	4	33	13	2100	35
Diesel automobiles	7	2	14	6	70	1
Air traffic	0.1	<0.1	<0.1	<0.1	—	—
TOTAL	295		250		6000	

estimated to produce 20 times as much PAH as either Norway or Sweden. However, if the populations of the U.S., Norway and Sweden are estimated to be 250.5 million, 4.3 million and 8.5 million[41], respectively, the amounts estimated become 23.95, 68.60, and 29.41 M.T. PAH emitted per million capita per year, which show that the United States' emissions on a per capita basis are actually less than either Sweden or Norway and that Norway produces the most per capita.

10.1.4 Emission Factors:

A method to compare PAH emission sources is to define what is called an emission factor. That is, to determine an important parameter for a certain PAH producing process and dividing the amount of PAH formed by this parameter (e.g. amount of fuel burned). This gives a weighted value of emission strength that can be compared between different processes. However, this method has limitations in that the same definition is not always possible. Also, when overall emissions are compared, one can be lead to different conclusions. For example, process A may emit less PAH per gram of fuel than process B, but process A may use a substantial amount of fuel more than process B so in fact, process A is a more significant polluter. If one looks solely at emission factors, one may conclude that process A is the more environmentally acceptable. Nevertheless, the use of emission factors still allows for comparisons of process efficiency with respect to PAH emission as long as the limitations are kept in mind.

Tables 10.4a to 10.4d list emission factors for various processes and are of interest since many may be potential candidates for use of waste oil as a fuel. Table 10.4a gives emission factors for residential heating with different fuels. The emission factor here is defined as mg PAH per kg of fuel consumed. With this definition, coal-fired furnaces emit a fairly high amount of PAHs, namely 60 mg/kg while the lowest emission is from a 30kW oil-fired burner. Note that for coal-fired processes, the range of PAH emitted varies a great deal. This is due to coal having different emission factors for different types and qualities of coal used, as well as differences in combustion systems used. The combustion of wood and coal give significant emission factors since combustion during these processes is often slow and incomplete.

Table 10.4b gives PAH emission factors for industrial sources defined as g PAH per ton of product produced. As you can see, this emission factor's definition differs from the one from residential heating (Table 10.4a) and therefore, makes direct comparison between the two much more complicated. Nevertheless, within the industrial sources of PAHs listed, the aluminum smelting industry has the highest emission factor, i.e. 235 g per ton of aluminum produced. The iron works industry is another significant producer of PAH with an emission factor of 60 g/ton. These industries probably use a lot of coal in their processes for fuel, which would account for the high emissions. Again, one can notice that the ranges of emission factors vary significantly, resulting from differences in detection methods as well as differences in operating conditions in various locations.

Table 10.4c gives emission factors for power and heat generators defined as μg/kg of fuel used. The most significant emitters in this area are hot water boilers fueled with wood and peat. Here again, combustion of these fuels is usually slow and incomplete,

Table 10.4a: PAH Emission Factors for Residential Heating[38]

Source	Range (mg/kg)	Typical (mg/kg)
Wood stoves	1-370	40
Fireplaces	----	29
Coal furnaces	1-1200	60
Oil (30 kW)	0.006-0.75	0.15
Oil (7.5 kW)	0.9-21.6	10

TABLE 10.4b: PAH Emission Factors for Industrial Sources[38]

Source	Range (mg/ton)	Typical (g/ton)
Aluminum smelting	$2\times10^5 - 6.5\times10^5$	235
Anode baking	-----	50
Coke production	-----	15
Petroleum catalytic cracking		
No control	1.4 - 3200	0.03
CO waste heat boiler	0.32 - 2.4	0.001
Carbon black production	220 - 490	0.3
Asphalt production		
Air blowing	2.8 - 4100	0.05
Shingle saturators	1 - 50	0.005
Iron and steel sintering	-----	0.34
Ferrous foundries	-----	7.7
Ferroalloy industry	-----	10
Iron works	-----	60

TABLE 10.4c: PAH Emission Factors for Power and Heat Generation[38]

Source	Range (µg/kg)	Typical (µg/kg)
Pulverized coal-fired power plants	0.5 - 32	19
Coal-fired fluidized bed	36.000[a]	---
Coal-fired industrial boilers	-----	41
Oil-fired industrial boilers	5.3 - 100	23
Oil-fired commercial boilers	-----	820
Gas-fired intermediate boilers	490 - 1100	1000
2 MW hot water boiler		
Wood	1180 - 3390	2000
Peat		15000

[a] The plant was not operated properly.

TABLE 10.4d: PAH Emission Factors for Incineration and Open Fires[38]

Source	Range (mg/kg)	Typical (mg/kg)
Incinerators (US, geometric mean)		0.017
Incinerators (2-5 tons/day)		6.8
Open burning		
Automobile tires		240
Municipal refuse		1.4
Forest fires	3.5 - 31.5	20
Agricultural burning		20

accounting for the high levels of PAH emitted. An interestingly low PAH emission factor is obtained from pulverized coal-fired power plants, i.e. 19 μg/kg. This number is interesting because a high value (60 mg/kg) was obtained in Table 10.4a for coal-fired furnaces which may lead to the conclusion that pulverizing coal before combustion, ameliorates combustion efficiency and lowers PAH emission. Oil-fired processes vary in PAH emission factors, demonstrating the lack of control with respect to PAH emission.

Table 10.4d gives emission factors for incinerators and open fires. Note that incinerators produce relatively low amounts of PAH per kg of fuel used. (However, this is a good example of the potential limitation of the emission factor since, in one day, a tremendous amount of fuel may be burned which would mean that the overall PAHs emitted would be high.) The greatest emission factor from this list is from the burning of automotive tires (which again follows from the slow and incomplete combustion processes involved). Note also the rather high emission factors of forest fires and agricultural burning (both giving factors of 20 mg/kg), which are uncontrolled processes.

For the reasons described above, it was deemed very important to understand the behavior of PAH release from used oils under the conditions currently studied. If a newer method of used oil disposal is to be ultimately proposed, PAH behavior will have to be addressed. Therefore, initial attempts at studying PAHs released during the slow heating process were undertaken.

10.2 Analytical Methodology

10.2.1 PAHs in Oil:

In order to observe PAH behavior, Oil 2 was spiked. Oil 2 was selected since it was sampled at an oil collection center and therefore was believed to be a sample more representative of used oils. By comparing the behavior of the spiked oil to the unspiked oil, it was hoped to isolate the PAH behavior in the environment being studied in order to propose future work on these important compounds.

Oil 2 was spiked with a 50000 μg/ml (ppm) standard of naphthalene and benzo(a)pyrene in a dichloromethane (CH_2Cl_2) solvent in order to get an oil sample with ~5000 ppm of each spiked PAH. Initially, a standard with pyrene and anthracene in addition to those mentioned above was attempted. However, the mixture could not be prepared since the solvent could not dissolve that high a concentration of four PAHs. Naphthalene was selected since it is the simplest PAH with only two benzene rings and has a low boiling point (i.e. 218°C) thus decreasing the chances of it condensing in the transfer line. Benzo(a)pyrene was selected since it is a compound that has been found to be carcinogenic[39] and has a boiling point (496°C) that was thought to be sufficiently far from that of naphthalene so as to isolate the effects of each PAH on the overall process.

In order to verify the concentration of the PAHs in the spiked oil, it was necessary to analyze both the spiked and the unspiked oil. This was done by using Thin Layer Chromatography preparative plates (TLC). The TLC glass plates are 10 cm by 20 cm and have a 0.25 mm silicone layer adhered to one of the flat sides. The oil sample being analyzed, as well as a reference PAH standard, are placed at the bottom of the plate which is lowered in a vertical position into a tank. A solvent is placed in the tank (50/50 iso-octane/cyclohexane) so that only a few centimeters wets the lower part of the plate. As the solvent slowly migrates up the silicone-covered plate, different fractions of the oil will migrate at different rates so that by the time the solvent reaches the top of the plate, the PAHs in the oil should be separated from any interfering compounds. The plate is then removed from the bath and allowed to dry.

When the plate is dry, it is placed under an ultraviolet lamp which allows the PAHs in both the standard and the sample to become visible in the form of a light blue hue. The area around the oil sample corresponding to the height where the standard PAH migrated is marked off and taken off the plate by scraping. This silicone, which contains any PAHs from the oil sample, is then crushed and extracted with a dichloromethane solvent. The solvent is vaporized under an inert atmosphere, leaving only the PAHs. Acetonitrile is added having an internal PAH standard of 2-methyl anthracene. This mixture is then injected into an HPLC for analysis. The TLC procedure allows for removal of substances that would otherwise interfere with PAH analysis.

10.2.2 PAHs in Gas-Phase:

Since PAHs were not detected by FTIR, PAHs were studied by using an organics trap (Orbo 100 Adsorbent Tubes) to capture the emissions generated and identifying individual PAHs by extraction and subsequent HPLC analysis. It should be noted that extractive sampling procedures may make detection of reactive species difficult.[23]

Prior to discussing results obtained in the PAH study, it is necessary to discuss the extraction procedure utilized. The organic trap is a cylindrical tube, tapered on the ends, having a diameter of 7 mm and 12 cm long. It contains 175 mg of carbonaceous particles that capture the PAHs from the gas-phase emissions through adsorption. Once the trap has been used, the two ends are covered with snug-fitting caps and the entire trap is wrapped with aluminum foil. This keeps the captured volatile material from escaping and also keeps the light away from the volatiles that are susceptible to reaction with light. The trap can be stored in this way for a period of time, until the extraction procedure can be completed in the laboratory.

When several runs are completed, the organic material from the traps can be extracted. One end of the trap is cut open so as to disperse the contents into a 10 mL vial. Five mL of benzene are added to the particles to extract the PAHs. The benzene/particle mixture is then placed in an ultrasonic bath for a period of 15 minutes. After the 15 minute period is over, the solution is homogenized using a Vortex vibrating instrument. The vial is then placed back into the ultrasonic bath for another 15 minutes of ultrasonic treatment, after which the Vortex treatment is repeated.

After this extraction to transfer the PAHs from the solid particles to the benzene solvent, the vials are allowed to sit for approximately 5 minutes so that some of the larger carbon particles settle to the bottom. Once done, as much of the liquid content as possible is transferred into a filter syringe (using silver lined filters to remove the fine carbon particles). The sample is then forced through the filter into another vial. The remainder of the liquid, as well as the solid particles, from the sample is then also passed through the filter to get the remainder of the benzene solvent and thus, the remainder of the PAHs.

Once the benzene solvent containing the PAHs has been filtered, an aliquot of the sample is transferred to a longer test tube and the amount taken is noted by marking off the level in the tube. The benzene solvent is then evaporated under nitrogen until only a small drop of liquid remains (thus leaving the PAHs in the vial). Once the evaporation process is complete, the vial is refilled to the marked line with acetonitrile solvent which includes an internal standard of 2-methyl anthracene. (This is done in order to maintain the same PAH concentrations as in the benzene solvent, which was initially 5 mL). This solution is then placed in a capped dark GC vial and placed in a refrigerator to await injection into the HPLC column.

10.2.3 HPLC:

All samples analyzed for PAHs were injected into a HPLC in the form of an acetonitrile solvent containing 12.025 µg/mL of 2-methyl anthracene, which was used as an internal calibration standard. 10 µL of the sample was injected using an ICI autoinjector, model LC1610. The HPLC was equipped with two columns in series (Supelco LC-PAH, 25 cm, 5 µm) which were maintained at 32±1°C. Gradient elution was accomplished with the following solutions: (A) 60% acetonitrile/water; (B) 100% acetonitrile (with a profile of 100% A for 10 min; 50% A for 10 min; 20% A for 12 min; 100% B for 6 min). The flowrate was 2.0 mL/min. The fluorescence detector utilized was linked via an interface (Hewlett-Packard, model 35900) to a PC equipped with a data handling program (Hewlett-Packard, Chemstation). For quality control, a sample blank and a standard mixture of 19 PAHs were analyzed after every 10 samples injected.

10.3 Experimental Procedure

The trap was set at the exhaust outlet and the sampling accessories removed. In this way, all emissions released would be passed through the trap and increase the amounts of PAHs captured. In order to minimize condensation prior to the trap, a larger vacuum pump was utilized to pull the emissions through the exhaust and minimize the opportunity for condensation. (During the runs, condensation was seen accumulating in the entrance to the organic trap. In the subsequent extraction procedure, it was found that at least a portion of this condensed material was not soluble in acetonitrile and thus was not PAHs. However, it is not known if some PAHs were condensed with this material but any results obtained include the condensed substance.)

Samples were run in this way on the spiked oil as well as on the unspiked oil, under the same conditions. The trap contents were then extracted and analyzed by HPLC and the spiked oil results compared to the Oil 2 results to determine the behavior of the

PAHs added. It is necessary to stop the heating process at a desired furnace temperature and remove the trap. Any PAHs found in the trap are therefore an accumulation over the heating period studied. At this point, not much was known about PAH behavior in this type of experiment and therefore, the temperatures of the initial study were selected as the same as those used for the solid phase study, i.e. 400°C, 650°C and 1000°C. Since naphthalene's boiling point is 218°C and benzo(a)pyrene's boiling point is 496°C, it was considered a reasonable approach for an initial study to use these temperatures since the processes for each PAH were likely to be isolated. Based on the results obtained from this study, a more appropriate set of experiments could be designed in the future to better understand the PAH evolution during the heating process.

10.4 Results

10.4.1 PAHs in Oil:

The results obtained from the analysis of both the unspiked (i.e. Oil 2) and spiked oils are shown in Table 10.5. Although Oil 2 was spiked with enough naphthalene and benzo(a)pyrene to give a sample with ~5000 ppmv of each, the analysis showed a complete absence of naphthalene and a lower-than-expected amount of benzo(a)pyrene (i.e. 33.40 instead of ~ 5000 ppm). Since the analyses were completed after experimentation, most of the spiked material was lost prior to analysis. (The results from the extraction experiments show that naphthalene was still in the spiked oil at that time, although the amount is unclear.) Naphthalene is very volatile and was most probably vaporized while benzo(a)pyrene, although not as volatile, is known to be more reactive and therefore, probably degraded, possibly forming other PAHs. This is a possible explanation since a few of the PAHs found showed an increase in the spiked oil. In particular, the increase in benzo(e)pyrene from < 0.13 to 2.26 ppm is probably due to the degradation of benzo(a)pyrene over time. Since only naphthalene and benzo(a)pyrene were added in the presence of a solvent, the concentration of all other PAHs was expected to decrease since the oil was being diluted with respect to these compounds (e.g., anthracene went from 10.82 to 6.23 ppm; phenanthrene from 43.52 to 34.72 ppm) and

Table 10.5: PAH Content In Oils Studied

PAH	Unspiked, ppm wt	Spiked, ppm wt
Naphthalene	< 0.13	< 0.19 *
Anthracene	10.82	6.23
Phenanthrene	43.52	34.72
Chrysene	< 0.38	< 0.57
Benzo(a)anthracene	0.75	0.75
Pyrene	17.23	18.87
Dibenzo(a,h)anthracene	< 0.03	2.83
Benzo(a)pyrene	< 0.01	33.40 *
Benzo(e)pyrene	< 0.13	2.26
Acenaphthene	< 0.13	< 0.19
Fluorene	14.47	6.98
Fluoranthene	10.94	9.06
Benzo(k)fluoranthene	< 0.02	< 0.02
Benzo(b)fluoranthene	1.38	1.13
Benzo(g,h,i)perylene	< 0.03	< 0.04
Indeno(1,2,3-cd)pyrene	< 0.10	< 0.15

* spiked

thus any increase in PAH content came either from the PAHs spiked or from their degradation (e.g. pyrene concentration rose slightly from 17.23 to 18.87 ppm).

10.4.2 Weight Behavior:

Once the Oil 2 sample was spiked with naphthalene and benzo(a)pyrene in a dichloromethane solvent, the spiked sample was studied under the same conditions as for the previous experiments and compared to Oil 2 results. A typical weight curve obtained from the spiked oil runs is shown in Figure 10.2 and is compared to an unspiked Oil 2 experiment. (Note that the results shown are from runs having exactly the same setup as previously described; i.e. the regular FTIR sampling accessories were in place and not the external pump/organic trap setup. It was not known how the external pump would affect the weight curve and balance system and therefore, the weight behavior was compared in runs having the regular setup for both samples.)

As can be clearly seen in the weight curves in the figure, the weight curve for the spiked oil is similar in shape but different in location than the typical Oil 2 curve. The spiked curve has a more significant initial weight loss and then seems to be shifted to the left in the area of the curve previously designated as the Major Weight Loss Zone (see

Figure 6.2). The shift is approximately 35°C in this zone, which is dominated by the bulk vaporization of the lighter liquid hydrocarbons present in the oil.

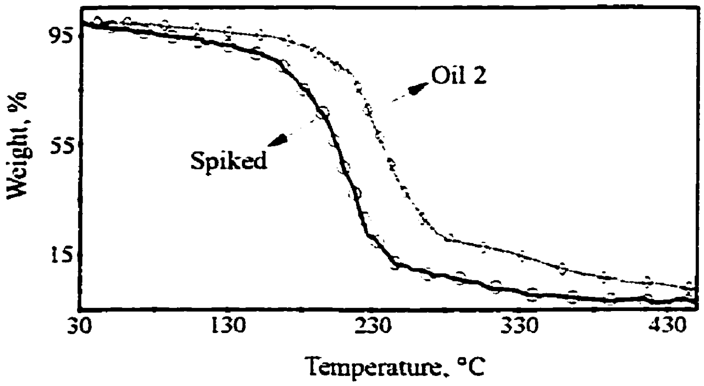


Figure 10.2: Spiked vs Unspiked Weight Behavior

It is not clear at this point why the difference is seen. After confirming that thermocouple placement was correct and that the shifting tendency was consistent in all runs, the FTIR data collected was analyzed. Unfortunately, the data collected was insufficient and inconclusive with respect to explaining the phenomenon seen. However, some hypotheses can be raised based on the observations and other knowledge. The only differences between the two samples are the two PAHs and the solvent which were added with the standard mixture when the spiked sample was prepared. Therefore, it is logical to conclude that some, or all, of these compounds affect the process and cause the difference.

It is clear that the initial weight loss difference is due, at least in part, to the evaporation of the solvent used to prepare the spiked oil (which was about 10% by volume of the spiked sample). This was confirmed with FTIR data which showed a dichloromethane peak from the onset of the heating to a temperature of approximately 90°C, as shown in Figure 10.3. However, the solvent evaporation temperature range corresponded only to a portion of the initial weight difference. It was not evident whether the solvent began to react after 90°C or whether no more solvent was found in the sample. All that was clear from the FTIR data was that pure solvent was no longer seen after this temperature. It was also seen that some naphthalene evaporated between 80°C and 150°C, although the identifying peak was very weak.[43]

The solvent may be the cause of the temperature shift. Chlorinated solvents such as dichloromethane have low boiling points which may lower ignition temperatures in oils

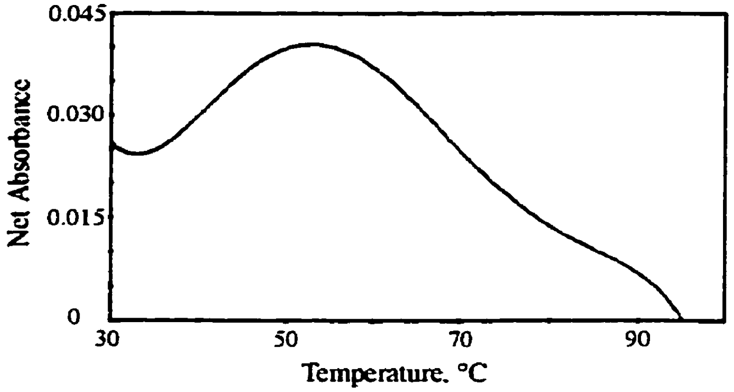


Figure 10.3: Solvent Evolution Profile

subjected to typical combustion processes.[44] Therefore, despite much of the solvent evaporating prior to the Major Weight Loss Zone, it is possible that the chlorinated solvent could still affect the vaporization temperatures of some of the hydrocarbons present in the oil mixture. This would cause the vaporization temperatures to be lowered and result in an apparent shift in the overall weight curve.

The PAHs added may also be the cause of the shift, especially since some naphthalene is detected just prior to the Major Weight Loss Zone of the process, where the shift is most noticeable. It is hypothesized that, as the added PAH oxidizes, the exothermic reaction increases the local temperature of the material inducing reactions to take place that would otherwise occur only at a later furnace temperature. Therefore, it is possible that the addition of hydrocarbons may increase the local temperature of the oil which would promote other reactions taking place at a lower oven temperature and would shift the weight curve since this would cause a chain reaction.

At this juncture, the above theories are hypothetical. Therefore, more work needs to be done in this area of the study to understand what is occurring. To do so, it would be necessary to isolate the three compounds added with the standard (i.e. add one compound at a time, to the oil matrix) in order to first determine which compound or compounds cause the shift to occur. Once that is identified, then further studies can be undertaken to attempt to explain why and how the effect manifests itself. Whether the effect is due to the solvent or the PAHs (or some combination), this can be a very important area of future study especially since the overall character of the weight-temperature profiles is very similar, excluding the shift phenomenon.

10.4.3 Gas-Phase PAHs:

The results from the extraction experiments on the unspiked and spiked oils are shown in Table 10.6 below. The extracts were analyzed for a total of 16 PAHs. The table shows the results for both oils at 400°C, 650°C and 1000°C in terms of mg of PAH generated per kg of oil used.

Table 10.6: Unspiked and Spiked Oil PAH Emission Factors, mg/kg oil

PAH	Unspiked			Spiked		
	400°C	650°C	1000°C	400°C	650°C	1000°C
Naphthalene	119.92	124.50	32.16	251.67	280.00	247.50
Anthracene	2.41	3.04	4.44	1.68	5.37	5.48
Phenanthrene	23.75	28.50	38.34	12.63	29.42	32.42
Chrysene	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Benzo(a)anthracene	0.02	0.02	0.07	< 0.01	0.05	0.07
Pyrene	5.35	7.41	10.6	1.72	7.24	10.36
Dibenzo(a,h)anthracene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Benzo(a)pyrene	< 0.01	< 0.01	0.06	0.77	3.37	3.85
Benzo(e)pyrene	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Acenaphthene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Fluorene	7.44	10.70	16.74	4.72	9.08	11.12
Fluoranthene	1.95	2.18	3.71	1.03	2.64	3.28
Benzo(k)fluoranthene	< 0.01	< 0.01	< 0.01	0.03	0.17	0.28
Benzo(b)fluoranthene	0.04	< 0.01	0.16	< 0.01	0.15	0.20
Benzo(g,h,i)perylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Indeno(1,2,3-cd)pyrene	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02

In general, the emission factors for the unspiked oil were higher than those for the spiked oil for the PAHs other than those added. Since when preparing the spiked sample a solvent was also added, other PAHs are expected to be diluted. For most of the PAHs, the amount generated increases with temperature, with the most significant amount being generated before 400°C. The patterns seen for each individual PAH are repeated for both unspiked and spiked oils, within some experimental error. However, for benzo(k)fluoranthene, which was not added to the spiked material, there is a significant increase in emission factor for the spiked oil. This may show that this PAH is formed during the heating process.

Figure 10.4 shows the evolution pattern of emission factors for naphthalene, benzo(a)pyrene and fluorene. Naphthalene and benzo(a)pyrene are the PAHs spiked while fluorene represents a typical behavior seen of the remaining PAHs detected. The naphthalene emission factor increased significantly (i.e. by over a factor of two) from unspiked to spiked sample. This increase shows that, at the time of experiments, the spiked oil sample still had significant amounts of spiked material despite there not being as much when the spiked sample was analyzed. However, in both cases, at 1000°C, the amount of naphthalene generated decreases. Since the collection process is continuous from 30°C to the collection temperature, the decrease in emission factor signifies that the naphthalene generated is reacting in the organic trap between 650 and 1000°C. The organic trap was not wrapped during the run and thus, the contents may have been exposed to ultraviolet light causing the naphthalene to react. In future experiments, it will be necessary to cover the trap even during the runs to prevent such reactions from occurring. As it was done for these experiments, it is not known whether the increases in other emission factors at 1000°C are due to formation from the process or from degradation of naphthalene.

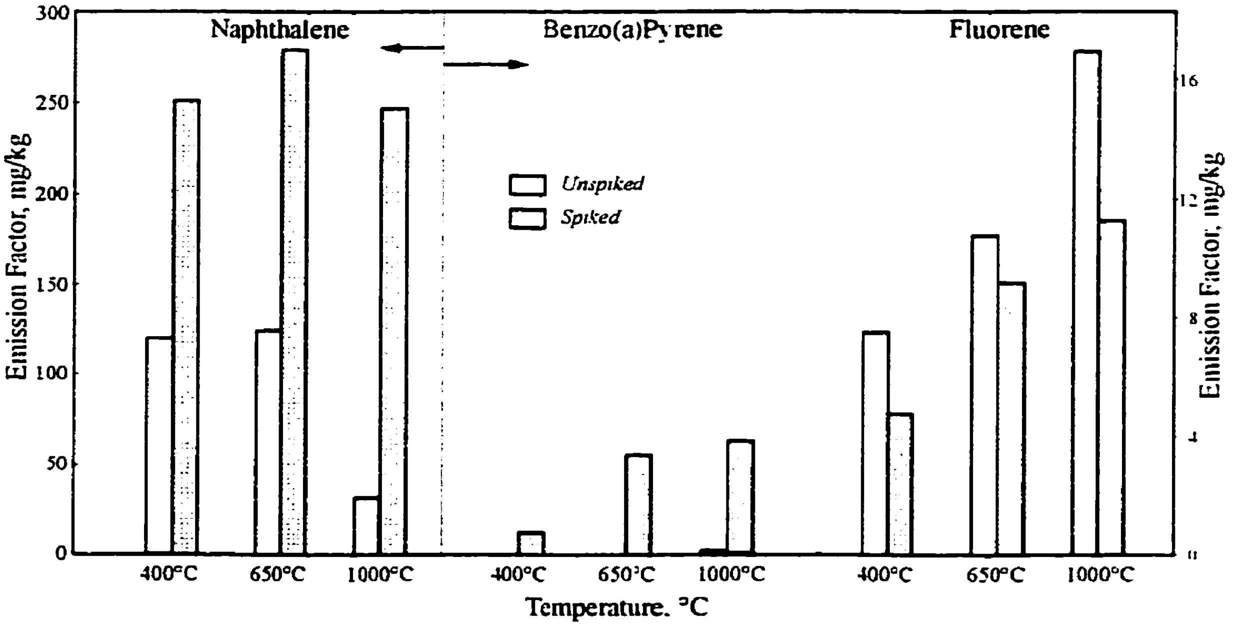


Figure 10.4: PAH Emission Factor Evolution

In terms of benzo(a)pyrene, Figure 10.4 shows that there was an increase in emission factor with benzo(a)pyrene content as well as with temperature (at least in terms of the spiked oil which was expected because of benzo(a)pyrene's higher boiling point). The unspiked oil generated a very small amount of benzo(a)pyrene. Fluorene showed the pattern of most of the other PAHs detected in that the emission factor increased with temperature but decreased from unspiked to spiked oil.

The initial experiments into the release of PAHs show that, during the process, many PAHs are generated in various amounts. Therefore, further study into the release of PAHs is warranted. However, the results obtained show that sufficient naphthalene is generated from the unspiked oil that it is unnecessary to spike the oil with naphthalene. The selection of benzo(a)pyrene as a PAH for spiking proved to be good since none was emitted from the unspiked sample. For future studies, the sample can be spiked with other PAHs, particularly those with low emission factors, to continue to study their behaviors. The results obtained show that several PAHs are generated during the oil combustion process. Some of these (such as benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene) are known carcinogens and their release is a concern to be addressed in practical combustion systems.

Chapter 11: Conclusions

The purpose of this study was to observe and understand the behavior of used motor oils during a slow heating oxidative process. Based on the results obtained, it is clear that it may eventually be possible to recommend more efficient and safer thermal remediation techniques to deal with the abundance of waste oils generated. It was believed that by first studying the behavior of a slow process, more information would be gained into the transformation of the oil that could be used in later studies of more typical combustion processes.

1. Under the conditions studied, the two oils were found to behave in the several distinct zones which were characterized by different dominating events. Following an initial heating period where very little occurs, the oil loses the majority of its mass due to volatilization of the liquid hydrocarbons present. In addition, there is also some limited oxidation taking place. After this vaporization, there is a transition zone where the sample changes from liquid to solid. In this stage, the material is tar-like and the rate of the process is affected significantly by the initial presence of elemental oxygen in the oil sample. Finally, once the transition zone has passed, the material becomes individual solid particles which continue to oxidize as the temperature increases. The onset of solid particles showed differences in initial structure for the two oils studied. The subsequent solid particle evolution was also clearly different and was due to different mechanisms occurring (surface oxidation for Oil 1 and both surface and internal oxidation for Oil 2).
2. It was clear by the observations made that the initial oxygen content of the oil sample played an important role in the transformation and combustion process. The presence of a significant amount of oxygen in Oil 2 affected the transition zone. The rate of oxidation during this transition was not disturbed noticeably in Oil 2 whereas the rate significantly slowed during the transition zone when initial oxygen was lacking. This is explained by the fact that, for Oil 1, oxygen required for the oxidation process of the transition material is limited to that available from the external environment. For Oil 2, the process does not slow down since some oxygen is also available from within the particle to continue the oxidation process.

3. Since the transition zone is affected by oxygen presence in the initial oil, the formation of the solid particles in the subsequent zone are also affected. For Oil 1 (no oxygen), the initially formed particle is flat and continuous (i.e. few pores). For Oil 2, the particle is smaller, partially coiled and more porous (since the transition zone is faster, the initial particle is surely formed earlier and has time to oxidize partially by 400°C). Due to the differences in initial structure, Oil 1 particles demonstrate mainly surface oxidation without a significant size reduction, while Oil 2 particles demonstrate both internal and surface oxidation causing the final particle to be more compact with a continuous surface and having a significant reduction in final size.

4. From the understanding of the oxidation process studied, it is probable that used oil is indeed a good candidate for use in practical combustion systems. The fact that a significant reduction in waste mass and volume is achieved was confirmed in the study. In all cases, the weight loss was always greater than 98%. What was also seen, however, was that during slow heating, the process clearly can be separated into different phases, namely a part where the sample reacting is liquid, one where the sample is solid and one where the sample is in transition. If this separation of phases during the process can be maintained in a practical thermal remediation unit, it could have significant implications from an environmental point of view.

5. Based on weight behavior of the oil sample studied, it does not seem necessary to operate the process at a very high temperature to achieve waste mass and volume reduction. It was clear that by 650°C, the samples had lost over 97% of its weight. Although in terms of environmental concerns, the effect of doing so is not clear, perhaps operating at a lower temperature would reduce energy requirements while still accomplishing the desired mass and volume reduction.

6. From a methodology point of view, it was clear that using the combined TGA-FTIR experimental setup proved to be very valuable in understanding used oil behavior. It allowed different aspects of the process to be studied while also allowing the flexibility necessary to develop the study method utilized. It can also allow for some parametric studies to be done as a follow up to the work already done in order to further the knowledge of the important aspects of the process. It turned out to be very important that

the process be slowed down for study. The slow down allowed for the observations that led to the realization of the importance of initial oxygen content on the process. In a faster combustion process, the process would occur so rapidly that perhaps the effect of oxygen could not be determined.

7. A number of Polycyclic Aromatic Hydrocarbons, PAHs, were identified (e.g., naphthalene, phenanthrene, pyrene, fluorene) which were released from Oil 2 during the process studied. When the oil was spiked with naphthalene and benzo(a)pyrene, the PAHs released increased for the two that were added while the amount of other PAHs, such as benzo(k)fluoranthene, also increased. This signifies the possible formation of PAHs not previously existing in the sample. Naphthalene was found to be very reactive and thus care needs to be taken when sampling in order to minimize its reaction with ultraviolet light.

8. There are different environmental concerns associated with volatilization of liquid hydrocarbons compared to those dealing with oxidation of solids. If the combustion process can be separated into its two phases (liquid and solid), it can allow for control strategies on each phase individually to minimize the particular environmental concerns associated with each phase. If this can be accomplished through the design of a continuous combustion system having a low temperature zone for the liquid oxidation followed by a high temperature zone for the solid oxidation, it can make environmental control of combustion processes much more efficient. The process parameters during the liquid phase of the process can be altered to concentrate solely on minimizing the emissions of unburned toxic compounds released. Once all the liquid is reacted, the combustion parameters can be adjusted to deal with solid phase environmental issues such as particle leachability since the gas-phase study showed that the solid part of the process does not release much in terms of hydrocarbons into the atmosphere. It is most likely that the eventual solution will involve a compromise between altering the process parameters to deal with the vapor phase pollutants and altering the process parameters to deal with solid phase environmental issues. Since practical combustion processes would probably involve faster heating rates, it may not be possible to separated the process into the liquid and solid aspects. Nevertheless, the possibility remains interesting.

Chapter 12: Recommendations

In order to continue the work done to date, there are a number of aspects of the process that still need further investigation. These can be separated into two classifications that are inter-related: those involving study of different environmental concerns associated with the process and those involving parametric studies to isolate the affects of different parameters on the process. Some of these studies can be combined.

1. First of all, environmental concerns need to be addressed in any new combustion design. Future work should focus on things such as PAH behavior, which was started in this work, in order to better understand the mechanisms involved during the oxidation of these hazardous compounds. This could be accomplished by performing more experiments with the organic trap sampling system at the same temperatures, to ensure reproducibility of the data obtained so far. In addition, since it is clear that much of the PAH release occurs below the first temperature utilized for the current study, i.e. 400°C, it is necessary to take samples at lower temperatures in order to determine the temperature ranges associated with PAH release. In addition to these PAH studies, it will also be beneficial to determine the types and amounts of other hydrocarbons released during the process, including PAHs associated with soot particles. Since it was not possible to identify those hydrocarbons, it will be important to do so if a more detailed understanding of the mechanisms occurring in the liquid oxidation part of the process is to be possible, namely whether the hydrocarbons result from direct vaporization from the sample or whether they result from partial oxidation. (This will be particularly important if hazardous products of incomplete hydrocarbon combustion are to be minimized.)
2. In a similar respect, since emission toxicity is a concern in practical combustion systems, it follows that mutagenic studies of emissions from this process be undertaken. The final environmental aspect to be addressed in future work involves the behavior of metals. Metal behavior also needs to be understood and taken into account in any new combustion system. Specifically, the leachability of metals in the final solid material produced should be investigated.

3. However, in order to address environmental concerns, process parameters need to be investigated to see what effect they have on the different areas of concern. This can be accomplished via various parametric studies. To better understand the overall process, it is necessary to confirm the importance of initial oxygen content (to ensure that an unknown factor such as metallic catalyst is not responsible for the differences seen). This can be achieved by artificially varying the oxygen content on the same oil and subjecting to the same conditions. Also, a parametric study on the heating rate will allow insight into more practical combustion systems as well as determining if control of heating rate can aid in lightening the environmental impacts of the process. Finally, parametric studies are required to continue the study on PAH behavior. It is necessary to isolate the three compounds added to the oil sample (i.e. dichloromethane, naphathalene and benzo(a)pyrene) in order to explain the shift in weight temperature profiles observed. Once this is understood, operating parameters can be altered in order to determine effects on PAH emission to ultimately minimize their release and formation.

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