OIL REFINING PROCESS

The invention relates to direct contact heating of normally liquid hydrocarbons and the like, especially those which are thermally unstable or difficult to heat, e.g., processing used motor oil to recover distillable and non-distillable hydrocarbons.

BACKGROUND OF THE INVENTION

Automotive and many industrial lubricating oils are usually formulated from paraffin based petroleum distillate oils or from synthetic base lubricating oils. Lubricating oils are combined with additives such as soaps, extreme pressure (E.P.) agents, viscosity index (V.I.) improvers, anti-foamants, rust inhibitors, anti-wear agents, antioxidants, and polymeric dispersants to produce an engine lubricating oil of SAE 5 to SAE 60 viscosity.

After use, this oil is collected from truck and bus fleets, automobile service facilities, municipal motor oil recycling centers and retail stores. There is also a significant volume of oil collected from the industrial sector, e.g., cutting, stamping and coolant oils, which is collected on a direct basis or is collected from oily-water dehydrating facilities. This collected oil contains organo-metallic additives such as zinc dialkylthiophosphate from the original lubricating oil formulation, sludge formed in the engine, and water. The used oil may also contain contaminants such as waste grease, brake fluid, transmission oil, transformer oil, railroad lubricant, crude oil, antifreeze, dry cleaning fluid, degreasing solvents such as trichloroethylene, edible fats and oils, mineral acids, soot, earth and waste of unknown origin.

Reclaiming of waste oil is largely carried out by small processors using various processes tailored to the available waste oil, product demands, and local environmental considerations. Such processes at a minimum include partial de-watering and coarse filtering. Some more sophisticated processors may practice chemical demetallizing or distillation. The presence of organo-metallics in waste oils such as zinc dialkylthiophosphate results in decomposition of the zinc dialkyldithiophospnate to form a carbonaceous layer rich in zinc and often other metals such as calcium, magnesium and other metals present as additives makes such waste oils difficult if not impossible to process. The carbonaceous layer containing the various metals forms rapidly on heated surfaces and can develop to a thickness of more than 1mm in 24 hours. This layer not only reduces the heat transfer coefficient of tubular heaters rapidly, it also results in substantial or total occlusion of these tubes within a few days.

CONFIRMATION COPY

Successful reclaiming processes require the reduction of the organo-metallics (or ash) content to a level at which the hot oil does not foul heated surfaces. Such reduction can be carried out by chemical processes which include reacting cation phosphate or cation sulfate with the chemically bonded metal to form metallic phosphate or metallic sulfate. In US 4,432,865, Norman discloses contacting used motor oil with poly-functional mineral acid and polyhydroxy compound to react with undesired contaminants to form easily removable reaction products. These chemical processes suffer from attendant disposal problems depending on the metal by-products formed.

Ash content can also be reduced by heating the used lubricating oil to decompose the organo-metallic additives. However, indirect heat exchange surfaces cannot be maintained above 200 - 205°C for extended periods without extensive fouling and deposition of metals from the additives. Used lubricating oils can be heated to an additive decomposition temperature of 205 - 540°C by direct heat exchange by mixing with a heated oil product as disclosed in US 5,447,628, Harrison, et al. However dilution of the product oil with used oil requires reprocessing already processed product oil...

UOP's Hy-Lube process, described in US 5,244,565 and US 5,302,282, and many more patents, uses hot circulating hydrogen as a heating medium to avoid deposition of decomposed organo-metallic compounds on heating surfaces.

The problem of fouling of heated surfaces can be ameliorated to some extent by gentler heating. Some processes, such as the fixed bed version of catalytic cracking, the Houdry process, used a molten salt bath to provide controlled, somewhat gentle heating of vaporized liquid hydrocarbon passing through tubes of catalyst immersed in the salt bath. Molten metal baths have also been used as a convenient way to heat difficult-to-process substances to a control temperature, e.g., flammability of some plastics is tested by putting a flask with plastic into a bath of molten metal. Use of a molten salt bath, or a molten metal bath, or a condensing high temperature vapor, could reduce uneven heating of heat exchange surface and thereby reduce dT across a metal surface and perhaps slow the fouling of metal surfaces in ULO service, but the additives in the ULO would still tend to decompose on the hottest surface, which would be the heat exchanger tubes.

Although not related to ULO heating, there has been use, either commercial, or reported in the patent literature, of molten metal for direct contact heating of various substances. The

float process for making glass is almost 50 years old. Molten metal, primarily lead, heating of coal or shale has been practiced in one form or another for almost 100 years. There are patents on use of molten metal baths for waste pyrolysis, and conversion of latex, by heating ground up plants in a metal bath to make an oily overhead product. Also somewhat related, but different from anything discussed above, is the HyMelt ® process, using a molten iron bath for dissolution of various feed stocks. Temperatures in the HyMelt process are so high that if a liquid hydrocarbon feed is fed to a HyMelt reactor, the feed almost instantaneously dissociates in hydrogen and carbon, with the carbon dissolving in the molten iron. This is an excellent process for dissociating a hydrocarbon into elemental constituents, but is overkill for reprocessing ULO, when all that is needed is enough heating to vaporize the lube boiling range components.

JP 59-124,991, in Ex. 1, used a molten metal bath to thermally crack ULO, preferably ULO with water added, to form a cracked vapor and a carbonaceous solid residue. The cracked vapors were condensed to form something like pyrolysis naphtha. The solid residue was removed from contact with the molten metal bath by a screw conveyor.

Some researchers took the position that fouling of metal surfaces during ULO processing was going to happen, and that the best way to deal with it was to inject something into the ULO which would scrub the metal clean, i.e., injecting an abrasive material.

Solvent extraction with light paraffin solvents such as propane, butane, pentane and mixtures thereof have been practiced by Interline and others. Details of the Interline Process are provided in US 5,286,380 and US 5,556,548. While the extraction approach seems like an elegant solution to the problem of processing ULO, the process may be relatively expensive to operate. Their quarterly report of May 15, 2002, reports that "It has become evident that demanding royalties based on production is impractical in many situations and countries. Unless and until the re-refined oil produced in a plant can be sold at prices comparable to base lubricating oils, collecting royalties based on production will be difficult. This reality was experienced in Korea, where the royalty was terminated for the first plant, and in England where the royalties were reduced and deferred until the plant becomes profitable."

A breakthrough in ULO processing occurred with direct contact heating of the ULO with steam or a non-hydrogenating gas. This approach solved the problem of zinc additive decomposition fouling of hot metal surfaces, by ensuring that the metal surfaces holding the ULO were always relatively cool. The hottest spot was the point of vapor injection. Decomposing additives had only themselves to condense upon. Such a vapor injection ULO process was disclosed in my earlier patent, US 6,068,759, *Process for Recovering Lube Oil Base*

Stocks from Used Motor Oil, and in US 6,447,672, *Continuous Plural Stage Heated Vapor Injection Process for Recovering Lube Oil Base Stocks from Used Motor Oil.* Other variations on the theme of ULO vapor injection processes are disclosed in US 6,402,937, *Pumped Recycle Vapor* , and US 6,402,938, *Vaporization of Used Motor Oil with Non-hydrogenating Recycle Vapor.*

The "state of the art" of used motor oil processing could be summarized as follows:

Chemical additive and extraction approaches can be used to react with, or extract everything but, zinc additives. High costs, and low reliability, have prevented much commercial use.

Indirect heating in a fired heater causes rapid fouling of metal surfaces. Using milder heating, molten metal or molten salt heating medium, can minimize but not eliminate fouling on hot metal surfaces.

Direct contact heating with high pressure hydrogen may eliminate fouling but requires high capital and operating expenses. Direct contact heating, with recycled product oil, helps but requires processing the ULO twice.

Thermal cracking by direct contact with a molten metal bath can be used to crack the ULO into lighter, cracked products and solid residue, but such approaches thermally degrade the light product.

Direct contact heating with steam or non-hydrogenating vapor works but is not the optimum solution.

Direct heating with steam, as reported in my US 6,068,759, was a good solution, but not perfect. When steam is injected, the process can create a water disposal problem and is thermally less efficient because latent heat of steam is lost when the steam is condensed. When, for example, propane is injected, large volumes of vapor are needed to provide sufficient heat input, and costs increase to heat and recycle such vapor streams.

I wanted an even better approach to re-refining ULO and other thermally unstable feeds. I wanted to retain the beneficial features of heating the ULO by injecting something hot into it, but avoid the problems created by using either steam or a light hydrocarbon vapor as the heating medium. I found a way to overcome these deficiencies, by using a non-pyrolizing molten fluid as the heating fluid.

BRIEF SUMMARY OF THE INVENTION

Accordingly, the present invention provides a method of refining used lubricating oil (ULO) having lubricant oil boiling range components and thermally decomposable additives comprising heating said ULO by direct contact heat exchange with a non-pyrolyzing molten fluid selected from the group of molten metal and molten salt at a temperature and for a time sufficient to vaporize at least a portion of said lubricant boiling range components and removing as a vapor product said lubricant boiling range vaporized hydrocarbons.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a simplified schematic drawing of a preferred embodiment wherein used oil is refined by direct contact heating with a continuous phase of molten metal.

FIGURE 2 is similar to FIGURE 1, but differs in that ULO, rather than molten metal, is the continuous phase.

FIGURE 3 shows an embodiment with a dehydration station upstream of the molten metal heating zone.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In FIGURE 1, as-received Used Lube Oil (ULO) flows from a feed storage system, 10, through line 12 to the feed pump, 13, into the contactor vessel, 14, at or near its bottom. A molten metal or molten salt heat transfer fluid, 15, that is immiscible with and much denser than ULO circulates from the bottom of the contactor vessel,14, by line 16 to a heater,18, that heats the heat transfer fluid to the desired temperature. Heating may also be accomplished by operating electrical resistance elements in the heat transfer fluid phase in the contactor vessel, 14. The heat transfer fluid flows back to the contactor vessel by line 20. Flow of the heat transfer fluid through the heater, 15, may be by natural convection, as shown, or the fluid may be pumped through the heater, 18, by use of a pump, not shown. The total liquid level in the contactor, 14, is maintained by a vertical outlet pipe, 22, through which all gas, vapor and liquid leave the vessel and flow through line 22, to the separator vessel, 26. The inventory of heat transfer fluid sets its level in the contactor, 14. When the level of the heat transfer fluid, 15, is relatively high as shown in Figure 1, ULO is the predominately dispersed phase and the heat transfer fluid is the predominately continuous phase. When the level of the heat transfer fluid is

relatively low as shown in Figure 2, ULO is the predominately continuous phase and the heat transfer fluid is the predominately dispersed phase.

The liquid and vapor entering the residue separator vessel, 26, separate into a liquid stream, 28, and a vapor stream, 32. The liquid stream, 28, flows to a residue storage system 30. The vapor stream, 32, flows through a cooler, 34, that may use air as shown in Figures 1 and 2 as the cooling fluid or some other cooling media such as boiling water, cooling water or some other fluid. The outlet temperature of the cooler 34 should be low enough to condense substantially all of the oil in the feed, 10. Usually an outlet temperature of less than 65°C causes nearly all of the feed to condense. The condensed stream flows by line 36 to an overhead separator vessel, 38, where any water in the feed, 10, separates and flows out through line 40 to a water storage system, 42. Liquid oil in stream 36 flows out through line 44 to an overhead oil storage system, 46. Any non-condensable gases flow out through line 48 to a gas handling system, 50. For low flows of non-condensable gas and when the operating pressure of the overhead separator vessel 38, the gas handling system may be a simple vent. For larger flows, a flare, or some other appropriate gas treatment system may be required. The gas handling system may be a vacuum system so the contactor, 14, the residue separator, 26, and the overhead separator 38 operate at sub-atmospheric pressure.

Figure 3 shows a more preferred embodiment of the subject invention. Feed ULO, 10 flows by line 12 to a charge pump, 13 to a partial condenser, 50, that heats ULO by partially condensing vapor from the overhead separator vessel, 42, to a temperature of about 175 - 180°C. The heated feed flows through line 14 to a pressure-reducing valve, 16, and then to a flash vessel 18. All water and approximately 1% of the hydrocarbons contained in the feed, 10, vaporize and flow by line 22 to a thermal oxidizer, 24, or some other appropriate treatment system where the hydrocarbons are converted to carbon dioxide and water and vented through line 26.

The dried feed flows by line 20 to the feed pump, 28, where it enters the bottom of the contactor vessel, 30, where it contacts heat transfer fluid, 31. The heat transfer fluid may be the continuous or dispersed phase as described earlier. The vertical outlet pipe, 32, maintains the total liquid level in the contactor vessel, 14. All gas, vapor, and liquid exit the contactor through line 34 to the residue separator vessel, 42. Liquid residue flows through line 44 to a residue storage system 46. Vapor flows through line 48 to the partial condenser, 50, where it is partially condensed by heating the feed as described earlier. The partially condensed vapor flows through

line 51 to a cooler, 52, where it is cooled to about 65°C by heat exchange with a cooling fluid. The resulting condensed stream flows through line 53 to the overhead separator, 54. Overhead liquid flows out by line 56 to an overhead storage system, 58. Any non-condensable gases flow by line 60 to a gas handling system. The gas handling system may include a vacuum system so that contactor, 30, residue separator, 42 and overhead separator, 54 operate at sub-atmospheric pressure.

DESCRIPTION OF PREFERRED EMBODIMENTS

Any molten fluid can be used which is immiscible with the ULO (or other oil) feed and which is reasonably stable in use. Molten metal is preferred, in part because this material has such a high thermal conductivity, and there is a wealth of operating experience associated with molten metal baths, although for other purposes. There are several metal alloys available which are fluid at relatively low temperatures which have ideal properties for use herein. They are non-corrosive. They are highly conductive, permitting compact furnace design to heat the metal. The metals are dense and carry of lot of energy per volume of fluid, so the used lubricating oil (ULO) re-processing plant can be small. They are not volatile, so they do not contribute to air or water pollution. They have a high surface tension, which means that decomposition products and trash found in the ULO will not stick to or stay with the molten metal, permitting extended use of the metal bath. Molten metal also permits a flexible design approach, permitting injection of the metal into the oil or vice versa, though not necessarily with equivalent results. When oil is injected into a molten metal bath, it is easy to increase or decrease process severity by changing the depth of molten metal in the bath or the temperature of the metal or the pressure in the molten metal bath.

Metals which can be used include lead, tin, antimony, mercury, cadmium, sodium, potassium, bismuth, indium, zinc, gallium. Preferably the metal used melts below about 300 - 325°C or forms an alloy that does. Not all metals will give equal results and some present significant safety concerns, e.g., lead or mercury, but they can be included as part of the molten metal bath, if desired.

Any feed containing a thermally unstable normally liquid hydrocarbon can be heated using the process of the present invention. The normally liquid hydrocarbons include C5 and heavier hydrocarbons, e.g., naphtha boiling range up through residual fractions which contain

sufficient olefins, di-olefins or other compounds to make them difficult to heat in a conventional fired heater. Heavy feeds, so heavy that they are not liquid at room temperature, e.g., a grease, wax, petrolatum or indeed any hydrocarbon having a high melting point may be used as feed. These materials will, upon heating, form liquids and may be used as feed. Treatment of solids is outside the scope of the present invention, i.e., treatment of coal or dirt contaminated with oil is outside the scope of the present invention.

What is essential for the practice of the present invention is direct contact heat exchange of a liquid feed with a molten fluid. The liquid must contain hydrocarbons. The feed usually will be contaminated with undesired lighter or heavier components which can be removed by heating, either to vaporize a desired feed component from a residue fraction or to remove an undesired lighter contaminant from a desired residue product fraction.

ULO will frequently contain both light and heavy contaminants. Light contaminants include water, naphtha and may include some impurities, such as solvents, introduced during the ULO collection process. Heavy contaminants include the additive package.

When processing ULO, the economic incentive is to vaporize as much of the feed as possible. There are usually two constraints on processing "severity" or on % vaporization. It is important to be able to remove the residue fraction from contact with the molten fluid by simply withdrawing it as a liquid. When processing ULO, the residue will not flow when more than 83 to 85% of the feed is vaporized. I believe that a practical limit is 80% vaporization of the dry oil. Another constraint is achieving vaporization, without undue product degradation. Degradation, or thermal cracking, can occur when either the overhead or the bottoms fraction is thermally cracked. When the overhead fraction is thermally cracked, there is a reduction in value. A potential lube oil rich fraction can be downgraded into pyrolysis naphtha by severe cracking of ULO feed, as occurred in JP 59-124991. The bottoms fraction can also be degraded by thermal cracking, as a residual liquid fraction has more value – and is far easier to remove – than a solid residual fraction. It is generally easier to overcrack the residue fraction, because this material can be left in contact with the molten fluid heating bath a long time, unlike the vapor fraction which typically has a much shorter residence time in contact with the molten heating fluid.

A surprising feature of the use of molten metal to heat ULO and vaporize the lube oil boiling range components therefrom, is that it is easy to achieve deep de-oiling of the ULO. The metal temperature at the bottom of a molten metal continuous bath and the oil temperature at the

top of the contactor, the oil floating on the surface of the molten metal, are very close. I have never seen more than 3°C difference in them, and there is no evidence of fouling.

The invention contemplates the use of a range of molten metals or molten salt for the high-intensity drying and/or heating process. These include low-melting point metal alloys. When simple drying or only a modest amount of thermal processing is desired, the candidate molten fluids may have melting points typically ranging from 60- 230°C.

It is essential that the heating fluid be immiscible with the ULO and substantially denser.

It is preferred that the interfacial surface tension between the molten metal heat transfer media, or other fluid which is immiscible with the feed being treated, and the liquid feed be sufficiently high to avoid sticking of the molten fluid to the wet surface. The thermal conductivity of the molten fluid should also be sufficiently high to ensure that the molten fluid remains in a liquid state, at least during the process, so that fluid does not solidify to form a solid film or freeze cone at the point of contact with the ULO.

When the thermal conductivity of the fluid is sufficiently high, the fluid conducts heat from the body of the molten bath to the interface contact region between drops or streams of ULO and molten heating medium, or drops or streams of molten heating medium when the ULO is the continuous phase. The use of molten metal alloys is preferred due to their high interfacial surface tension with decomposition products that may form from, and trash that may be found in, the ULO. Metals are also preferred over other immiscible fluids due to their high thermal conductivity. An additional benefit is the high density of molten metal relative to ULO, which promotes rapid transit of one fluid through the other and plenty of motive force should baffles or column packing be used.

Table 1 summarizes some estimated properties for several recommended molten metal eutectic alloy materials, when only moderate severity heating is required. This alloy information is taken from information reported in US 5,619,806, which is incorporated by reference.

TABLE 1

Properties of Candidate Molten Materials

	Melting Temp °C
In/Sn(52/48)	118
Bi/Pb(55/45)	124
Bi/Sn(58/42)	138
Sn/Pb(63/37)	183
Sn/Zn(92/8)	199
"Tin Foil" Sn/Cu(99/1)	227

The metallic material of the bath may consist of an alloy selected from the group that includes:

i) Ga/In

ii) Bi/In

iii) In/Sn

iv) Bi/Pb

v) Bi/Sn

vi) Sn/Pb

vii) Sn/Zn

viii) Sn/Cu.

A spectrum of molten metal temperatures can be used, from high to low. Based on the float bath process for making plate glass, tin has ideal properties when a relatively high temperature bath is desired. Tin has a melting point of 232°C and a boiling point of 2623°C. This means that a range of temperatures can be achieved in the molten metal bath, ranging from temperatures near the boiling point of water (when a low melting alloy like Wood's metal is used, to temperatures above 500°C. For ease of startup, i.e., a relatively low melting point, a tin-bismuth alloy is preferred.

EXPERIMENTS

The experiments were conducted in a length of about 10 cm ID (4" schedule 40) stainless steel pipe. The metal alloy used was a tin-bismuth eutectic that is 42% tin and 58% bismuth. The depth of molten metal was about 50 cm, with about 30 cm of freeboard or vapor space above the molten metal. The stainless steel pipe was heated by a cylindrical heater, an electric jacket with a thermostat. The initial series of tests on ULO was conducted at about 316°C molten metal bed temperature. The ULO feed was fed into the bottom of the molten metal bath via a 6 mm nipple to which a length of 3 mm SS tubing was affixed. The tubing did not extend into the molten metal bath. The process ran under vacuum, which is customary for lube oil recovery processes. I estimate that the pressure was about 0.5 - 1 psia, but the pressure gage used was not very accurate at these low pressures.

The first tests were run with a poor sample of ULO, which had about 10 wt % water, much more than is present in any automobile engine. I do not know where all the water came from, but it was there, and caused considerable processing difficulties, perhaps due to slugging addition of an aqueous phase, which caused the apparatus to shake and the metal to splash out. A significant quantity of metal was lost due to the unusual water level of the feed, but the process worked to vaporize lube oil components from the ULO.

The next set of tests was run after dehydration of the ULO feed, to remove essentially all of the water. This series of tests would approximate the process flow shown in Figure 3, i.e., dehydration before "distillation" of the ULO in the molten metal bath. The process worked smoothly, with none of the rumbling and spattering associated with the initial series of tests. The overhead product was a golden clear liquid, which looked almost like honey. There was some odor associated with both the overhead and the liquid residue, but the liquid residue had less smell than the ULO feed.

One problem was encountered in early runs, freezing of metal near the point of feed injection. This was overcome by adding some heat tape to the stainless steel tubing. This will probably not be a problem in commercial sized units, but if it is some form of heating of the feed injection means can be used to overcome it.

The experiments represent actual work done in a laboratory, but should not be construed as either a limitation on the process nor an optimization thereof. ULO re-refiners may operate at even lower temperatures, using a molten metal bath or molten salt bath merely to remove water and/or "light ends" which may be present. This mild use of the technology would permit a fleet operator to periodically condition the motor oil used in vehicles, by removing water and crankcase dilution, and return the conditioned motor oil to the vehicle, perhaps with some additional additives. Some re-refiners, especially those with no market for a heavy liquid residue product, may want to use higher temperatures to maximize production of distillable hydrocarbons and minimize production of a heavy "resid" liquid from the ULO. This use would simultaneously improve product recovery and minimize disposal costs.

DISCUSSION

The most surprising result, to me, of the experiments, was the low temperature difference between the top and bottom of the molten metal bath and of the residual liquid oil fraction, all were within about 3°C. In a conventional refinery process, using a metal walled heat exchanger or a fired heater with metal tubes, temperature differences at any point on the metal surface are typically 6 - 30°C with huge temperature differences between the inlet and the outlet of the device. As an example, if a fired heater was used to heat and vaporize a ULO feed, the oil feed temperature at, or just inside of the inlet to the heater, would be ambient, or perhaps 65°C if some heat exchange was practiced on the ULO feed. At the heater exit, the ULO would be at the desired process temperature, typically 260 - 400°C, and the temperature on the furnace side of the tube would be 290 - 485°C, to give enough ΔT to drive heat through the tube walls and into the ULO. Relatively large ΔTs are needed to reduce the surface area of heat exchange tubing, or heater tube, to an affordable amount. Heat transfer is relatively slow across a solid metal surface, the heat energy has to pass from the hot furnace interior by convection and radiation to the outer surface of the heater tube, through the metal tube (and this is typically efficient), across the interface between the inner tube wall and the layer of vapor/liquid in close proximity to the tube wall, and eventually into the bulk stream of ULO feed. There are many "pinch points",

which slow down the overall rate of heat transfer. Part of the problem in a fired heater is that the relatively hot metal tube surfaces cause vaporization and fouling, both of which drastically reduce heat transfer. Vaporization reduces heat transfer because it is roughly an order of magnitude more difficult to heat a gas than a liquid. Fouling reduces heat transfer because the thin, but growing, layer of carbonaceous deposits acts like an insulator, while providing a relatively porous place to hold hydrocarbon liquids and vapors a long time, permitting thermal cracking and more fouling.

In the process of the invention, especially when practiced with a metal bath continuous phase, the natural phenomenon which occur during heating become virtues rather than vices. ULO, when injected into the base of the bath, is almost instantly heated, causing some vaporization and disruption of any large droplets of ULO that may try to form. The ULO vapors produced are much lighter than the residual ULO liquid, and are believed to form something like a three phase bubble, with a vapor top and a liquid oil bottom in a molten metal shell. If a large bubble forms, the light vapor portion will either break away from the residual ULO liquid, or at the least cause some form of vigorous agitation as the large multi phase bubble rises. If the vapor portion breaks away, that leaves the residual ULO liquid to form a new bubble, but of liquid, or at least much more liquid than before the vapor phase broke away, and this denser bubble will not rise as quickly in the molten metal bath, giving more time for the molten metal to heat the ULO.

Radiant heat transfer is also believed to play a significant part, in that the lens shaped oil pool in the lower portion of a bubble has a large surface area to volume ratio, one or more orders of magnitude more favorable for heat transfer than can occur when the ULO passes through a metal tube of 10 – 15 cm or similar diameter, in a fired heater. Radiant heat transfer is considered to play a negligible part of transferring heat from a hot metal heat exchange surface to oil flowing within, or around, the surface. In my process, the bubbles are small and "see" enough hot molten metal so that significant radiant heat transfer occurs.

Based on the work done to date, the preferred metal composition is the tin-bismuth eutectic that is 42% tin and 58% bismuth. It looks like the optimum conditions for temperature and pressure will be around 315 - 330°C and 50 to 75 mm Hg pressure. There are actually an infinite number of temperature pressure combinations that will give the 80% overhead yield desired. For ULO, the limits on the combinations of pressure and temperature may range from

about 300°C at 0.5 mm Hg pressure to 425°C at near atmospheric pressure. Either of these extremes could result in an inoperable situation. The key parameter is vaporizing 75 to 80% of the feed without causing problems that make the process inoperable.

The ultimate use of the products, both the overhead lube oil fraction and the residue fraction, can have an important influence on operating conditions. When the process is being run to recover a high quality lubricating oil base stock, or a material which will receive further conventional processing to make it a base stock, relatively low temperatures and somewhat lower product recoveries may be optimum. When the residue product is going to be an asphalt extender, the desire is to preserve as much as possible of the plastic present in the ULO, primarily the viscosity modifier, to improve asphalt properties. When the overhead product will be FCC feed, a lower quality product can be tolerated, so higher temperatures and higher recovery may be optimum. To minimize production of low value waste, and this will usually be the residual fraction of the ULO, after the lubricant boiling range hydrocarbons have been removed, it may be important to have very high temperatures and/or lower pressures, to reduce the resid fraction as much as possible.

SALT BATH

When a molten salt bath is used, it is important to maintain reducing conditions during processing. Salt baths can be reactive, especially when used in an oxidizing atmosphere. Oxidizing atmospheres, if present during lube oil recovery, will degrade the quality of the lubricating boiling range hydrocarbons recovered overhead, so maintaining a reducing atmosphere is preferred.

When a molten salt bath is used for simple dehydration of ULO, or to remove light ends, such as naphtha or other materials sometimes present as "crankcase dilution" it is not so critical to maintain a reducing atmosphere, as the temperatures involved are usually so low that oxidation reactions will either not occur or occur so slowly as not to be troublesome.

Any salts heretofore used as a heat transfer medium may be used. Some common salts used in heat transfer are:

KNO_3, KNO_2, $NaNO_3$ and $NaNO_2$

Na_2CO_3, Li_2CO_3, K_2CO_3

NaF, ZrF, LiF, BeF_2

Often salts are combined to form eutectics or other lower melting mixtures such as Sun Salt; 60% $NaNO_3$ and 40% KNO_3 or Hi Tech XL; 48% $Ca(NO_3)_2$, 7% $NaNO_3$ and 45% KNO_3. Mixtures of Na_2CO_3 and K_2CO_3 have long been used in coal gasification and pyrolysis.

GENERAL CONSIDERATIONS

It is important to use a molten fluid, with a "heat range" within that required for the desired process objectives. When simple dehydration of ULO is all that is required, and this will usually be a first or preliminary treatment rather than the entire process, molten metal is preferred rather than molten salt, as the water in the feed may react with or dissolve in molten salt. For dehydration, molten metal which is molten in the 80°C+ temperature range is suitable. When distillation of lubricating oil boiling range components from the ULO is desired, the molten fluid must remain molten at temperatures above 100°C to about 600°C.

The upper limit on temperature/choice of the molten salt or molten metal is usually determined by volatility and process constraints. Preferred are molten metals or molten salts which have a low vapor pressure at the temperatures used, so that loss of molten metal due to "dusting" or for any other reason is less than 1% a day. The metals or salts chosen should not be corrosive under process conditions and preferably are non-toxic, for safety.

This invention permits drying and/or recovering lube oil base stocks and/or other hydrocarbons from used motor oil. The process and apparatus of the present invention also permits efficient processing of other waste or low value oil streams that contain so much emulsified water and/or additives that conventional processing is impractical.

When used to process ULO, this invention permits the separation of metallic additive packages from valuable distillable hydrocarbons in the waste motor oil with limited, or no, decomposition of these distillable hydrocarbons. When the residual fraction from the ULO is destined for use as an asphalt extender, it may be beneficial to have some or most or even all of the additive package intact. The plastic viscosity modifiers used in some lube oils may have beneficial effects in the asphalt, so it is good to have a process which gives re-refiners the option to decompose, or not decompose, the additive package.

The process and apparatus of the present invention may also be used to heat other thermally unstable, or difficult to heat, liquids.

While our tests were conducted at relatively low pressure, re-refiners may wish to operate under a harder vacuum, to maximize recovery of lube oil components and minimize

decomposition of additives. Others may wish to operate above 1 atm up to 100 atm pressure, or more, to minimize vapor volumes and facilitate processing of streams with large amounts of water. Higher pressures permit a more compact facility to be built.

The experiments were conducted using a single molten metal bath, but the invention is not limited to this embodiment. Multiple molten metal baths may be used, much as product fractionators use multiple distillation trays, each operating at a slightly different temperature.

Claims

1. A method of refining used lubricating oil (ULO) having lubricant oil boiling range components and thermally decomposable additives comprising:
   a. heating said ULO by direct contact heat exchange with a non-pyrolyzing molten fluid selected from the group of molten metal and molten salt to vaporize at least a portion of said lubricant boiling range components and
   b. removing as a vapor product said lubricant boiling range vaporized components.

2. The method of claim 1 wherein said molten fluid is maintained as a continuous phase.

3. The method of claim 2 wherein said molten fluid is disposed as one or more baths and said ULO is injected into, or bubbles up through, said molten fluid.

4. The method of claim 1 wherein said ULO is maintained as a continuous phase and said molten fluid is poured, sprayed or otherwise passed down through said continuous ULO phase.

5. The method of claim 1 wherein said molten fluid is molten metal.

6. The method of claim 1 wherein said molten fluid is maintained at a temperature of 100 to 600°C and said contact of said ULO with said molten fluid occurs under vacuum.

7. The method of claim 1 wherein said thermally decomposable additives are recovered as a liquid phase.

8. The method of claim 1 wherein said ULO fluid is dehydrated prior to contact with said molten fluid.

9. The method of claim 1 wherein from at least a majority to about 85 liquid volume percent of said lubricant boiling range hydrocarbons in said ULO are recovered as a vapor product.