

Lecture 11

Used Oil

1. Introduction



- Used oil generation is ubiquitous and it can contain hazardous liquid wastes and other contaminants
- When used lubricating oil qualifies as a HW, its disposal becomes complicated and costly.
- Burning as a fuel and re-refining are the two major methods for recycling used oil.
- Because of the constituents present in used oils, air emission controls may be necessary when burning.

● ● ● | 1. Introduction 

- Another use of lubricating oil is its re-refining back into a usable base base oil.
- In engines, oil becomes dirty and additives break down.
- Re-refining process concentrates contaminants into a bottom residue, which is reused in asphalt production.
- Re-refined crankcase oils meet or exceed the engine lubrication testing requirements for new oil.
- The re-refining of used oils is a preferred energy conservation and pollution prevention alternative

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● ● ● | 1. Introduction 

- Lack of a regulatory control and an infrastructure for the collection and processing results in improper disposal.
- To minimize the improper disposal of used oil, the management system must be modified:
 - To divert the improper disposal of used oil in refuse and the environment and get it into the used-oil management system of collectors, handlers and processors.
 - To correctly manage used oil after entering the system by including standards that address accountability
 - To increase the flow of used oil into re-refineries

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2. Terminology

USED OIL	
GENERATOR INFORMATION	
COMPANY	_____
ADDRESS	_____
CITY, STATE, ZIP	_____
SOURCE	_____
CONTACT	_____

- After collection, used oil recycling consists of a wide variety of activities yielding a range of products.
- Thus, it became necessary to appropriately define terms used to describe various recycling approaches.
- **Used oil:** oil that has, through use or contamination, become unsuitable for continued use in its current application, but which is likely to have some use in another application or as a feedstock for a process that generates a useful product.

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Used oil



- Spent engine lubricating oils and vehicle fluids:
 - automotive crankcase oil
 - diesel engine crankcase oil
 - natural-gas-fired engine oils
 - alternative fuel engine oils
 - transmission fluids
 - brake fluids and
 - power steering fluids.



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Used oil



- Spent industrial oils:
 - compressor, turbine, and bearing oils
 - hydraulic oils or fluids
 - metalworking oils or oil emulsions (cutting, grinding, machining, rolling, stamping, quenching, coating oils)
 - electrical insulating oils
 - refrigerator/air conditioning unit oils
 - rubber-making oils
 - cable oils; greases; and oil-like heat transfer fluids

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2. Terminology



- **Waste oil:** oil that has become so degraded or contaminated that it is impractical to recover anything useful from it other than its heat content.
- With the increased understanding of lubricant chemistry, focus on pollution prevention and enhanced recycling facilities, very little lubricant becomes waste oil.
- **Recycling:** covers all aspects of used oil collection, processing and reuse. Thus, reprocessing, reclaiming, and re-refining are all subsets of recycling.



RECYCLE
USED OIL

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2. Terminology

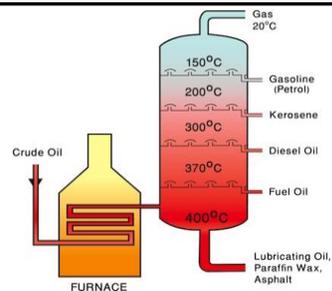


- **Reprocessing:** is producing fuels, whether for burning in small space heaters or large industrial boilers.
- This may include simple settling and filtration techniques to remove bulk water and solids.
- **Reclaiming:** is reconditioning a lubricant so that it can be reintroduced into the original application.
- Especially useful for hydraulic fluids and other industrial lubricants that have relatively simple compositions and less demanding applications.

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2. Terminology



- Reclaiming involves simple dehydration, settling and filtration techniques followed by additive replenishment.
- **Re-refining:** is production of a clean base oil equivalent to virgin base oil from which any and all petroleum-based lubricants can be blended.
- Involves sophisticated processing and testing.

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3. Oil Consumption



Methods of Estimating Oil Usage:

1. Engine oil is changed after every 5000 km drive.
This makes approximately 1 Lt of oil used per 100 Lt of gasoline purchased.
If annual motor vehicle fuel consumption is known.
Oil consumption can then be estimated based on motor vehicle fuel consumption.

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3. Oil Consumption



Methods of Estimating Oil Usage:

2. Since motor vehicles use more oil than any other application, motor vehicle registrations may be used to estimate engine-related oil consumption.
3. Estimating oil consumption using population data (liter per capita) is a simple and commonly used method.
But, population data may not exactly reflect oil users.

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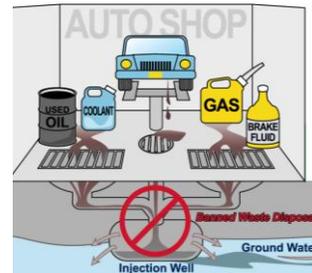
Used-oil generation factors

- A significant portion of engine oils are non-recoverable owing to combustion in the engine, residual left in engine components (oil filters) and unintended spilling.
- Generation factor is the volume of used oil generated compared with the volume of oil initially purchased.
- Generation factors for engine oil are considerably higher than for industrial oil because crankcase oil is changed more frequently.
- Engine oil generation rate: ~ 60% of annual purchase

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Disposal of used-oils



Used oil is improperly disposed of by:

- Direct disposal into the environment by dumping
- Collection with municipal solid waste with subsequent disposal in a landfill or incinerator
- Burning on site
- Disposal to a liquid effluent treatment system
- On-site secondary use such as a machinery lubricant or dust suppressant

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Waste oil categories

Category I

- pollutants such as PCB, total halogen & heavy metal are below the limit values
- recovery through refining & regeneration
- suitable for use as additional fuel in the facilities licensed by the Ministry

Category II

- chloride & total halogens: 200 – 2000 ppm
- PCB: 10 – 50 ppm
- suitable for use as additional fuel

Category III

- chloride & total halogens > 2000 ppm
- PCB > 50 ppm
- not available for refining
- create risks for human health and environment should be combusted & disposed

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Waste oil categories

Pollutants	Allowable Limit Values		
	Cat. I Waste Oil	Cat. II Waste Oil	Cat. III Waste Oil
Arsenic	< 5 ppm	max 5 ppm	> 5 ppm
Cadmium	< 2 ppm	max 2 ppm	> 2 ppm
Chromium	< 10 ppm	max 10 ppm	> 10 ppm
Chloride	max 200 ppm	max 2000 ppm	> 2000 ppm
Lead	< 100 ppm	max 100 ppm	> 100 ppm
Total halogens	max 200 ppm	max 2000 ppm	> 2000 ppm
Polychlorinated Biphenyls(PCB)	max 10 ppm	max 50 ppm	> 50 ppm
Flashing point	Min. 38 C	Min. 38 C	-

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4. Used Oil Handlers



- Persons who handle used oil are subject to specific management requirements depending on the extent of their used oil recycling activities.
- Handlers subjected to management standards are;
 - Generators
 - Collection centers and aggregation points
 - Transporters
 - Transfer facilities
 - Processors and re-refiners
 - Marketers



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Generators

- Used oil generators are persons whose act or process produces used oil.
- Common generators include car repair shops, service stations, and metalworking industries.
- Individuals who generate used oil through the maintenance of their own personal vehicles and equipment, known as used oil do-it-yourselfers 'DIYs'.
- DIYs are not considered used oil generators.

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Collection centers and aggregation points

USED OIL
COLLECTION
CENTER
RECYCLE FOR FREE!

Recycling your used motor oil is easy.

- 1 REMOVE.** Do not spill any oil on the ground.


 - Accept small amounts of used oil and store it until enough is collected to ship it elsewhere for recycling.
- 2 CONTAIN.** Put your used motor oil in a clean plastic container with a tight lid. Never store used oil in a container that once held chemicals, food or beverages.


 - Collection centers typically accept used oil from multiple sources that include both businesses & private citizens.
- 3 DO NOT MIX.**


 - Aggregation points collect oil from places run by the same owner and operator as the aggregation point, and also from private citizens.
- 4 RECYCLE.** Take used motor oil to a service station or other location that collects used motor oil for recycling.





Transporters and transfer facilities

- Transporters are persons who haul used oil in bulk quantities and deliver it to transfer facilities, re-refiners, processors or burners.
- Transfer facilities are any structures or areas (parking areas) where used oil is held for longer than 24 hours, but not longer than 35 days, during the normal course of transportation.



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Processors, re-refiners and burners

- Processors and rerefiners are facilities that process used oil so that it can be burned for energy recovery or reused.
- Processing generally includes: blending used oil with virgin petroleum products, blending used oils to meet the fuel specification, filtration, distillation or any activity that changes chemical/physical condition of used oil.
- Burners are handlers who burn used oil for energy recovery in boilers, industrial furnaces or incinerators.

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5. Hazardous Contaminants

Virgin Lubricating Oil Characteristics:

- New and used lubricating oils can contain hazardous constituents such as metals, chlorinated compounds, and polynuclear aromatic hydrocarbons (PAHs).
- New lubricating oil contains a combination of base stock oil and various additives.
- Virgin base stock oils contain metals such as barium, cadmium, lead, and zinc on the order of 0 to 1 ppm.
- Lesser amounts of Cr (0 to 0.05 ppm) and PAHs (<1 ppm) have also been identified.

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Lubricating oil characteristics



- Additive compounds enhance the effectiveness of lubricating oil and greatly influence its composition.
- They comprise 10-30% (by vol.) of engine oil products.
- Additives inhibit metal corrosion, oxidation of oil and act as detergents, dispersants and antiwear compounds.
- They contain hazardous constituents such as Mg, Zn, Pb and organics, and they also increase the concentrations of sulfur, chlorine and nitrogen in oil.

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Used-oil contaminants



- Used oils become useless not because hydrocarbons in oil have broken down, but because of a combination of additive depletion and contaminant accumulation.
- The combination of additive depletion and introduction of contaminants creates the potential for damaging the hardware being lubricated.
- High-quality base oil could be recovered with standard refinery techniques and therefore dirty lubricants can be cleaned up to their original condition.

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● ● ● | Used-oil contaminants

- Used oil contaminants include;
 - solids (sludge, varnish, rust and wear debris)
 - additive degradation by-products (oxidized additive molecules and sheared viscosity improver polymers)
 - water (free, emulsified and dissolved)
 - fuels and process chemicals.
- Once the used lubricant is awaiting collection and recycling, further contamination may occur.
- This secondary contamination is often more problematic and are not related to petroleum-based lubricant.

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● ● ● | Used-oil contaminants

- Typical parameters for used oil arriving at a processing plant might include:
 - Water content 10 to 30%
 - Flash point >100 °C
 - Acid number 2 to 3
 - Chlorine 500 to 3000 ppm
 - Sulfur 1000 to 4000 ppm
 - Non-distillables 5 to 15%

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Contaminants of special interest

- Water and sludge are contaminants that affect product quality, but do not contribute to any health concerns.
- There are, however, other contaminants present at much lower levels, which provide significant motivation for the controlled collection and disposition of used oils.
- Halogenated solvents that are often used as cleaning agents are found in used oil, although they are never components of lubricants.
- They are indicators of contamination of the used oil.

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Contaminants of special interest

DO NOT MIX.



- Ethylene glycol is widely used as antifreeze in automotive cooling systems.
- As such, it is another waste stream generated in the automotive services and is often found blended into used oils for disposal.
- Some modern used oil re-refineries isolate and market the ethylene glycol contained in their feed stream.
- Ethylene glycol is toxic and contributes to the overall toxicity of used oil.

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Contaminants of special interest

- Lead and benzene contamination in used oil originally came from gasoline that found its way into the oil as blowby in engines (mist pushed past the piston rings).
- After the elimination of lead in gasoline, lead content of used oils decreased significantly.
- The primary source now is additives and wear metal.
- Benzene is present at levels of 0.5 to 3% in gasoline.
- Any gasoline contamination incorporated into used oils contributes a volatile carcinogen.

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Contaminants of special interest

- Toxic heavy metals can be introduced during use or from contamination after use.
- Primary metals in used oil are As, Cd, Cr and Pb.
- Only Cr and Pb are found at above 1 ppm with any frequency, and both tend to be below 50 ppm.
- Advanced re-refining techniques can remove the carcinogenic properties of used oils as well as the heavy metals.

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Contaminants of special interest

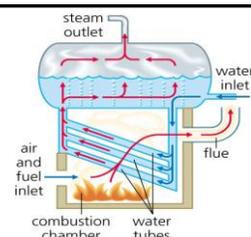
Concentration of potentially hazardous constituents in used automotive oil

Constituent	Number tested	Samples above detection limit, %	Mean concentration,* ppm	Median concentration, ppm	Concentration range, ppm		Regulatory limit for used-oil fuel, ppm
					Low	High	
Metals							
Arsenic	24	8	9.9	5	<5	14	5
Barium	113	95	209.5	94	0.78	3,906	
Cadmium	64	93	1.7	1	<0.2	10	2
Chromium	99	97	10.8	8	0.5	50	10
Lead	40	97	2,573.7	1,470	5	21,700	100
Zinc	116	100	982.3	1,000	4.4	3,000	
Chlorinated solvents							
1,1,1-Trichloroethane	22	18	401.3	6	<1	1,000	
Trichloroethylene	22	9	2.5	5	<1	16	
Tetrachloroethylene	22	36	180.1	9	<2	660	
Total chlorine	36	100	1,200.0	800	<100	4,700	4,000
Other organics							
Benzene	22	45	589.0	9	1	3,600	
Toluene	22	86	1,010.7	190	1	6,500	
Xylene	22	90	2,005.2	490	2	14,000	
Benzo(a)pyrene	21	100	9.7	10	1.3	17	
PCBs	22	5	39	—	—	—	

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Source: Tchobanoglous & Kreith, 2002

6. Typical Uses

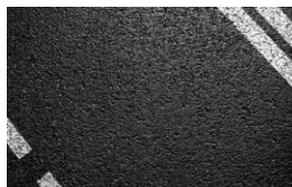


- After collection, used lubricating oil is used in or sold as feed for a variety of uses.
- The most prevalent use for used oil was fuel for energy recovery and dust control, such as road oiling.
- Since the 1990s, environmental legislation has ensured that road oiling with used oils has almost completely disappeared in developed countries.
- Today, the primary use worldwide is as a fuel.
- The collected used oil is burned for energy recovery in small furnaces and industrial boilers.

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6. Typical Uses



- Another widespread use for used oil is in asphalt.
- Some asphalt plants buy used oil for use as a substitute fuel with the residues incorporated into the asphalt.
- Asphalt manufacturers also purchase the vacuum distillation bottoms from re-refiners for direct blending into their product as an asphalt extender¹.
- Further, the asphalt binds trace metal contaminants to prevent leaching into the environment and volatile organics are consumed in the manufacturing process.

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¹ a substance added to another substance to increase its volume or bulk.

6. Typical Uses



- Of all the potential uses, re-refining (recycling used oil to produce lubricant base oil) is often viewed as the optimum pathway for used oil.
- By making a product that can be used over and over, re-refining saves a valuable natural resource while diverting a potentially HW from loss into environment.
- The modern re-refinery uses vacuum distillation like a crude oil refinery.
- Therefore, the quality of the products made from re-refined oils is equivalent to that made from virgin oils

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7. Technologies

- In-plant recycling of used oil is a specific form of reclaiming in which the life of the oil is extended.
- In-plant recycling steps are filtration to remove solids, heating to remove water and reformation of the depleted additives.
- If the performance requirements for the original application are too stringent, alternative uses can be found for the oil, for example, as a metalworking fluid.
- Regulatory paperwork is eliminated and process cost is reduced, because used oil is not transported off-site.

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7. Technologies



- In the used oil recycling hierarchy, re-refining to make high quality base oil is the highest level and requires the use of more sophisticated technology.
- When looking at the distillation characteristics of used oil, it becomes obvious that many of the contaminants can be removed by distillation.
- Base oil is the fraction boiling btw 315°C and 540°C.
- Many approaches to isolating commercially attractive lubricant products have been attempted over the years.

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Re-refining

- The re-refining process is >98% efficient in converting used engine & industrial oils into high-quality lubricants.
- Re-refining process consists of 4 steps
 1. Dehydration
 2. Defueling
 3. Extraction and distillation
 4. Hydrotreating



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Re-refining



- When waste oil arrives at a re-refining plant, it is first tested for contamination and then bulked and mixed in a storage tank to achieve a uniform feedstock.
- The first step, dehydration, is needed because waste oil coming into the plant can contain 12-15% water by vol.
- Oil is piped to the dehydration tank and heated to 135°C under atmospheric pressure.
- This boils off water and some lighter petroleum fractions.
- The wastewater produced is treated on site.

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Re-refining



- Then the oil is fed to the defueling system and the temp. is raised to 230°C under a vacuum of 100 mmHg.
- This process removes more light fuel and lubricating oils, which are then condensed and used as a fuel on site.
- In the next step, the oil is completely vaporized at 400°C under a vacuum of 3 mmHg and then condensed into three separate oil fractions and pumped to holding tanks.
- Of the material not collected, the lightest fraction is marketed as an industrial fuel.

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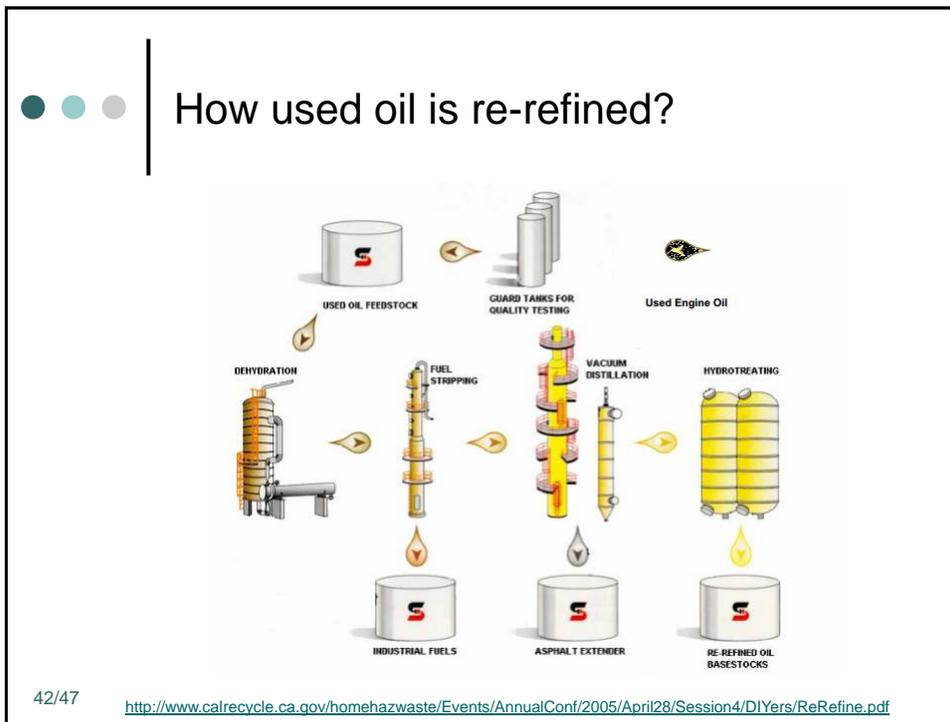
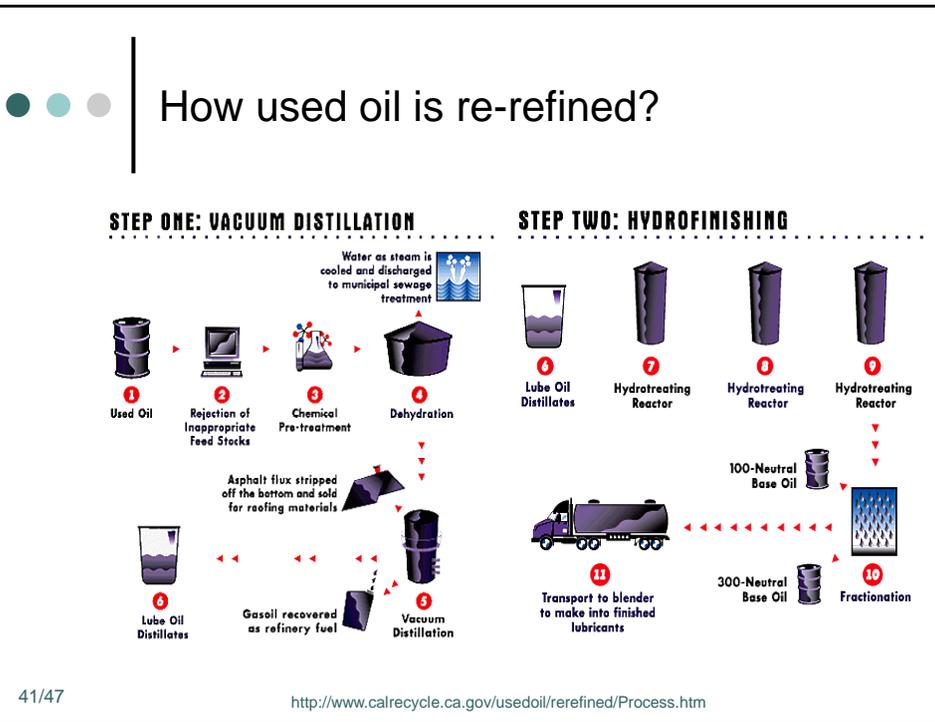


Re-refining



- The heavy fraction is marketed as an asphalt extender.
- This product contains the additives, polymers, wear metals, contaminants and oxidized materials.
- In the final step, each of the three distilled oils is fed into a reactor at high P and T with H₂ and a catalyst.
- This process removes S, N, chlorine, oxygenated compounds, heavy metals and other impurities.
- The end product of re-refining is base oil, which can be used to formulate new engine, gear and hydraulic oils.

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8. Environmental Issues



- Oil in any form is potentially harmful to the environment.
- Studies of oil spills indicate that it takes >20 years for an aquatic environment to return to a healthy condition.
- In aquatic communities oil residue tends to settle on the bottom and coats the substrate of organisms.
- When poured on the ground, it can rapidly migrate through the soil and contaminate the groundwater.
- In both instances, all living organisms experience physiological stresses.

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8. Environmental Issues



- Oil film on water can reduce the penetration of light and consequently, reduce the rate of photosynthesis.
- The oil film may also inhibit the movement of oxygen from the air through the surface of the water.
- The reduction of DO in the water stresses aquatic life.
- Oil can clog respiratory mechanisms and even be incorporated into the tissues of these organisms.
- These substances in the tissues of fish and shellfish make them unfit for human consumption.

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Regulatory methods to increase used-oil collection

- Impose regulations on the generators of used oil.
- Provide a deposit-refund system on the purchase and return of new and used oil.
- Provide a tax on engine-related purchases to subsidize used-oil collection and recycling.
- Require sellers of lube oil to maintain collection facilities.
- Develop a state-supported infrastructure of public and private collection centers.

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Regulatory methods to increase used-oil collection

- Rely on public education and labeling as a method of impacting end use.
- Use government procurement policies to stimulate the market for rerefined used oil.
- Require lube oil producers to reuse a certain amount of used oil (either through rerefining or as a fuel).

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Videos

- Waste Oil Refinery - System components
http://www.youtube.com/watch?v=C6Ew1qJ_26o
- How to Recycle Used Motor Oil
<http://www.youtube.com/watch?v=fmrD-yc6Gxc>
- The Used Oil Management Standards
<http://archive.org/details/gov.epa.530-v-99-001>