

USED OIL RECYCLING BY USING SUPERCRITICAL PROPANE

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A new process for used oil treatment was investigated, which uses compressed propane for the extraction of the oily fractions. It is demonstrated, that it is possible to clean used oils in compact plants at moderate pressures lower than 100 bar and with low energy consumption. The process is realised in a pilot plant with a capacity of up to 40kg/h of used oil. The gained product has a quality which allows its use in small local diesel driven power plants. If the extraction is combined in an integrated process with hydro-treatment in presence of propane even an oil quality is obtained, that is applicable as base oil for lubricants. Thermodynamic studies and integrated processes are presented which illustrate how the used oils have to be treated to get clean oils of high quality at a high yield.

INTRODUCTION

In Europe some million tons of used lubricants have to be disposed each year. Only a minor portion of these used oils are collected and are material- or energy-recycled. The major part is lost during processing. The collected oils are treated in few refineries or used as fuel in cement industry. Regarding ecology and economy, both paths of disposal are unsatisfying. The refinery process causes a high logistical and infrastructural effort and has a high energy demand for purification of the used oils. The combustion of used oils in the cement and heavy industry without any pre-treatment of the oils may result in uncontrolled pollution. The heavy metals, which are found in used oils, stay in the product (e.g. cement) or are to be found in the exhaust gas. Due to the disadvantages of the classical disposal of used oils, different research groups have investigated new possibilities to purify and recycle oils. A very promising method is the extraction of the oil components using supercritical gases [1,2].

THERMODYNAMIC BEHAVIOUR OF USED OILS IN PRESENCE OF DIFFERENT COMPRESSED GASES

For the extraction of oil components, compressed alkanes like ethane and propane seem to be most suitable. In first experiments the phase behaviour of used oils in presence of these gases was investigated. Therefore a high pressure view cell with a movable sapphire piston was used. This equipment allows to observe the phases which occur at different pressures and temperatures and offers the possibility to take samples to determine the composition of the phases. By moving the piston during the sampling the pressure stays constant, therefore a disruption of the phase equilibrium can be avoided. **Figure 1** shows the used view cell. The cell is suitable for pressures up to 800 bar and temperatures up to 250°C.



Figure 1: view cell to determine the phase behaviour

Both systems show good solubility of the gas in the liquid oil-phase. With increasing pressure the level of the liquid rises, caused by the dissolved gas. Even a high solubility of the oil components in the compressed gas can be expected at elevated pressures. The colour of the gas phase changes from transparent to light yellow. This is an indication for soluble components. If the pressure is raised further both components, the oil and the gas, become completely miscible. This is observed for ethane and propane either. The difference of both gases lies in the pressure level which is necessary to obtain a single phase. For ethane 233 bar are needed, against 61 bar for the system propane/used oil (see **figure 2**). Therefore the extraction process of the used oil might be realised at lower pressure, if propane is used.

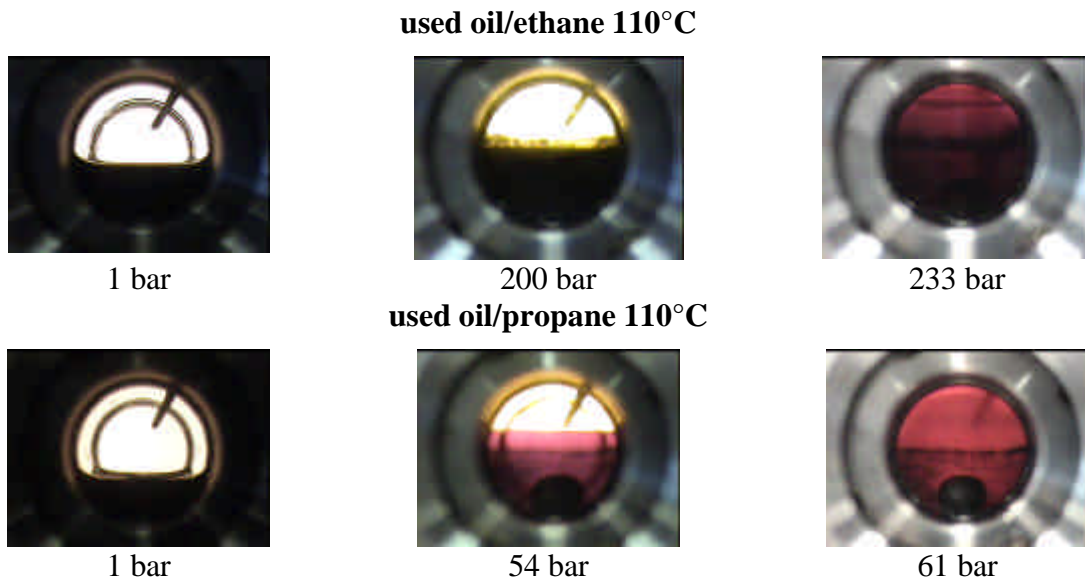


Figure 2: View cell photographs of the systems used oil/ethane and used oil/propane

To quantify the solubility of both components the composition of the gaseous phase and the liquid phase was determined. The measurements were achieved as static-analytic-method, by taking samples of both phases. The pressure in the cell was held constant by moving the sapphire piston during the sampling. The results for both phases are shown in **figure 3**. The single phase regime of both systems is suddenly reached by increasing the pressure less than two bar – the mixing gap runs very flat near the critical point of the mixtures. Therefore it was not possible to determine compositions near the critical pressure. It is obvious, that propane/used oil is the more promising system. Higher solubilities of the oil in the gaseous phase are reached at lower pressures. Resultant lower investment cost are necessary. To reach an acceptable gas ratio for the extraction process, mass fractions of more than 10 wt.% oil in propane are needed. The flat curve progression of the mixing gap, near the critical point, is more distinctive at lower temperatures. Therefore high temperatures of 150°C are favoured to

allow a stable controlling of the extraction column. Otherwise small pressure fluctuations in the column will led to a single phase behaviour and the separation will fail.

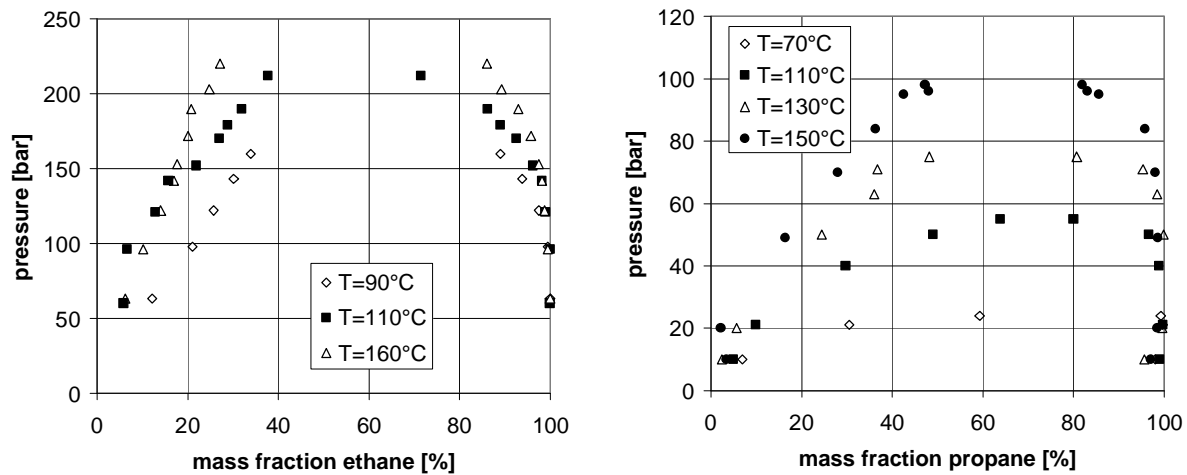


Figure 3: Phase behaviour of the systems used oil/ethane and used oil/propane

EXTRACTION PROCESS FOR USED OIL RECYCLING

Based on the thermodynamic behaviour described above, an extraction process for the recycling of used oil was developed. **Figure 4** shows a simplified flow scheme of the process. In a first step the used oil is heated in a vaporizer to separate water and low boiling components of the main oil fractions. The distillate has to be condensed in an additional vessel, which is not shown in this figure. The water-free oil is dosed with high pressure pumps to a packed extraction column. In a counter current flow compressed propane is used to extract the oil components. As described above, 95 bar and 150°C are the most suitable conditions for the extraction process. As a residue the heavy oil and solid components are withdrawn at the bottom of the column.

The extract is lead from the top of the column to a hydrotreatment unit. The temperature in this column is raised to 250°C. In this column hydrogen is added to the mixture of propane and oil components. The complete system stays in a single phase regime, which combines high yields and low hydrogen consumption. For the hydrogenation a heterogeneous catalyst is used. The reaction is handled in such a manner that the chlorinated organic compounds are transformed to hydrogen chloride and the sulphur compounds are converted to hydrogen sulphide. Even polyaromatic hydrocarbons (PAH) can be destroyed with this technique [3]. The separation of the organic compounds mentioned above, offers the possibility to form a high quality product which can be used as fuel in small diesel-driven power-plants, without any pre-treatment, as well as a base oil for the lubricant industry.

The process is completed with a separation unit which allows a nearly complete recycling of the extraction gas. In a first step the propane with the dissolved oil components and the products of the hydrogenation (HCl, H₂S) are depressurised to 18 bar into a vessel. A phase split occurs and the main product can be withdrawn at the bottom of the vessel. The gaseous phase has to be treated in an additional absorption column. Here a sodium hydroxide solution is used to wash out the chlorinated and sulphuric gases. A water phase with the dissolved salts Na₂S and NaCl is formed. The gaseous propane and some minor water leave the absorption column. To minimise the investment and energy costs of the process the propane has to be

liquefied before the recompression. This allows the use of an high pressure liquid pump instead of a gas compressor. In the heat exchanger the pressure is hold at 18 bar. This allows the use of water as a coolant. If the pressure is lowered to less than 18 bar a refrigerating set is necessary. By lowering the temperature three phases occur. One gaseous hydrogen phase, which can be reused in the hydrotreatment, one liquid propane phase which has to be recycled and one liquid water phase, which can be withdrawn at the bottom of the separation vessel. To close the extraction loop, a high pressure pump is installed to raise the pressure to 95 bar and finally another heat exchanger is necessary to set the temperature of the recycled propane [4].

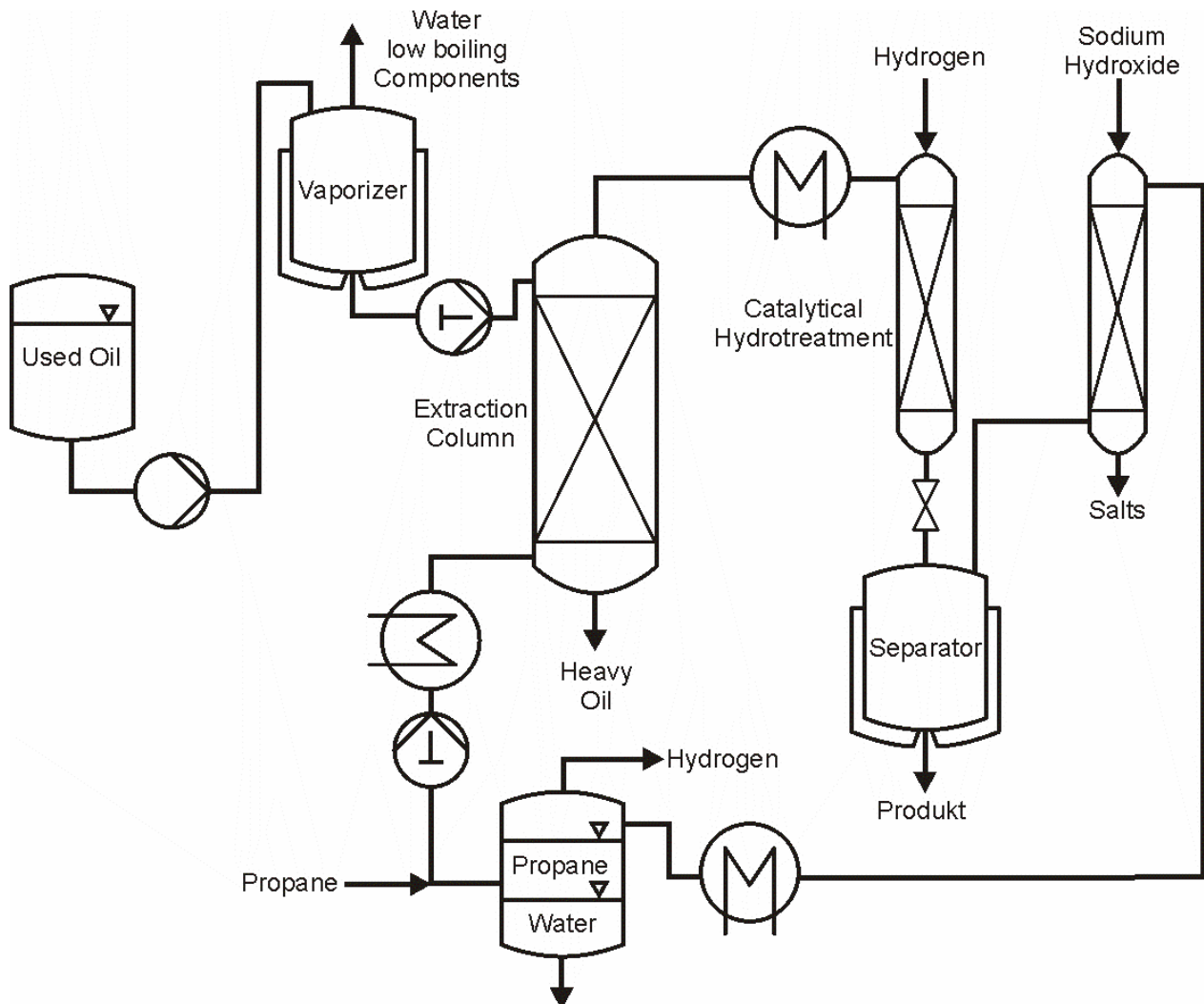


Figure 4: Simplified flow scheme of the extraction process

EXPERIMENTS

The view cell equipment described above was used to extract oil fractions from different used oils. Therefore the cell was filled with 24 ml of water-free used oil. Afterwards the cell is tempered to 150 °C and propane is dosed into the cell until a pressure of 95 bar is reached. To intensify the contact between the compressed gas and the oil, the stirrer integrated in the cell, is used for 10 min. After another 60 minutes both phases are completely separated again and the sampling is started. Small samples of both phases are withdrawn from the interior of the

cell. During the sampling the pressure in the cell is held constant by moving the sapphire piston. Pictures of the used oil, the raffinate-phase and the extract-phase are shown in figure 5. It is obvious that the main contaminations of used oils remain in the raffinate phase and therefore a deep black colour is observed for the feed, the used oil, as well as for the raffinate. In contrast thereto, a light golden extract phase is obtained. This indicates the purification of the oil fraction.

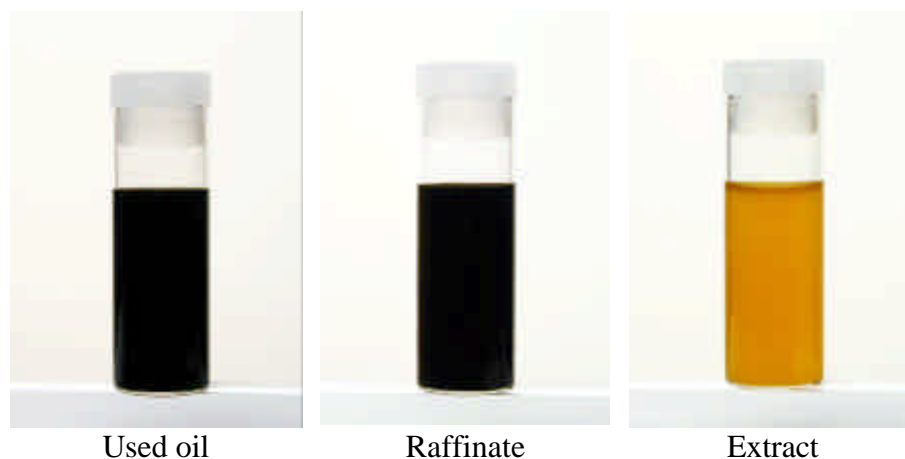


Figure 5: Samples of the used oil, the raffinate and the extract

Chemical analyses of the fractions showed, that most heavy-metals and most inorganic components, which are existent in high concentration in normal used oils, prefer to stay in the raffinate phase (see table 1). This allows to employ the extracts as substitutes for diesel in power plants, without any further treatment.

Component	Used Oil [mg/kg]	Extract [mg/kg]
iron	1661	2
chrome	14	1
nickel	185	3
copper	37	<1
lead	27	2
silicon	1170	24
calcium	1267	1
magnesium	255	<1
phosphorus	140	<1
chlorine	500	70
sulphur	3010	2760

Table 1: Chemical analysis of used oil and extract [5]

CONCLUSIONS AND OUTLOOK

In this research project a propane-based process for the treatment of used oil was investigated. With the determination of the phase behaviour of the used oils in presence of the compressed gas, promising conditions were found, which allow to operate the extraction plants economically. The extracts obtained with simple one stage extractions, are purified sufficiently to use the gained oils as high quality fuels. First results with an additional hydro-

treatment are even more promising. With this technique the concentrations of sulphur compounds and aromatic compounds are reduced significant [3]. Resultant a valuable oil, which can be used for lubricants is obtained. In further investigations a pilot plant with a capacity of 40 kg used oil per hour is operated and the engineering of an industrial plant with a capacity of 5000 tonnes per year is completed. Additionally the hydrotreatment unit has to be tested more intensively, especially the lifetime of the used catalyst has to be proofed. Finally different investigations are made to minimize the plant volume with the purpose to build mobile plants for used oil recovery. This would lead to a decentralised treatment of used oils directly at the industry sites where the oils are used and would contribute to higher material- or energy-recycling of oils.

ACKNOWLEDGEMENTS

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