A Review of Solvent Uses in Petroleum Industry

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Abstract

Oil is known as a major source of energy and an economical source of the word. However, depleting world’s crude oil resources has caused increase attention toward heavy oils and bitumen to supply the demand for fuels and petrochemical feedstock. Different techniques have been employed to extract crude and heavy oil with high possible efficiency. As conventional recovery methods currently used have become less efficient, solvent extraction seems to be a suitable alternative and a most cost-efficient recovery process for all recovery methods which requires no water and the solvent is recoverable and reusable. Solvent extraction followed by adsorption also has been found to be one of the competitive processes for recycling of used lubricating oil. Basis of solvent extraction is injecting diluents like naphtha or light oil and some vaporized hydrocarbon solvent, usually, ethane, propane, or butane to the pump to reduce the of the heavy oil to make pumping easier. The petroleum solvents are light section produced from crude oil which is containing paraffinic and aromatic hydrocarbons of petroleum in different ratios. It is obvious that solvent costs and availability are two important factors that determine the economics of such processes. This review paper was aimed to present some information about petroleum solvent and the process in which this solvent is used.

Keywords: Diluent; Heavy oil; Lubricating oil; Recovery process; Viscosity
Introduction

Solvents of varying volatilities contribute an important part of the petroleum industry to many manufacturing processes. Petroleum solvents are light section produced from crude oil which is containing paraffinic and aromatic hydrocarbons of petroleum in different ratios. These solvents usually have no color and it does not dissolve in water. Solvents have different applications for example: as resin dissolved in paint, adhesives and rubber industries. Also, they are used as intermediate in some chemical reactions and in extracting oil and aromatic material. Petroleum solvents are divided into 4 groups: 1) Special Boiling Point Spirits (SBP) with boiling point of 308-1608 °C 2) aromatic solvents like benzene toluene and xylene 3) White Spirits with boiling point of 150-210 °C 4) Kerosene-Type Solvent with boiling point of 160-300°C. SBP and white solvents are produced from crude oil distillation which other solvents are obtained by extraction, cracking, reforming and alkylation methods [1, 2]. It is obvious that solvent costs and availability are two important factors that determine the economics of oil processes. In spite of extensive literature, many books and numerous papers that have been done on solvents generally, their specific properties and the uses of these materials in individual processes there is almost no comprehensive information on the properties and applications of the petroleum solvents. So this present review was aimed to represent information in this field.

Solvent extraction

In definition is the distribution ability of a solute in an aqueous solution and an immiscible organic solvent. Organic solvent separates and purifies the solutes by extracting into the organic phase, leaving undesirable substances in the aqueous phase [3-5]. The solvent extraction technology has the potential to produce oil products more efficient than those that produced by the low-temperature distillation process. As it is known that the highest yield of any extraction process obtains by this technique and solvent extraction is one of the cheapest and most efficient processes in the recycling of used lubricating oil which requires no water, the solvent is recoverable and reusable. Studies have shown that n-hexane has good oil extraction ability on used lubricants [6, 7]. However Ahmad et al., 2008 study showed that n-hexane due to its low boiling point is the optimum solvent and toluene was found to be the second best extracting agent. While comparing toluene and Methyl-Tert-Butyl-Ether (MTBE) for extraction of oil from lubricating grease introduced toluene as suitable based on its higher 26 w/w% of oil recovery than 19.6% for MTBE.
However, SRS Engineering Corporation (2013) indicated that the extracting solvent must have two important abilities: 1) miscible ability with the base oil contained in the waste oil 2) rejecting from the solution the used oil impurities.

**Solvent extraction efficiency**

It had been shown that Solvent injection is the efficient EOR in different types of rock samples. The efficiency of solvent injection in different types of rock samples was tested by Hatiboglu and Babadagli (2008). More recently, Al-Bahlani and Babadagli (2010) introduced a new technique of solvent injection in fractured reservoirs as a steam-over-solvent injection (SOS-FR). The published experimental results of Al-Bahlani and Babadagli (2010) work proved that the possibility of solvent injection can be improved by providing the ability of solvent retrieval at the end of the process by injecting steam or hot water. In fact, the purpose of the SOS-FR method was finding an applicable solution to improve the efficiency of heavy oil/bitumen recovery from fractured carbonates and oil sands reservoirs after cold production [8]. Al-Bahlani and Babadagli (2008) measured solvent retrieval by using refractometer index and weight difference methods. They estimated solvent retrieval of about 85-90% at the end of the process. However, accurate measuring of the solvent retrieval is not quite simple as the solvent used is in vapor phase during its retrieval and therefore highly volatile. Dehghan et al. (2009) reported that displacement of oil by the solvent in the water-wet medium is more efficient than in oil-wet medium in the presence of connate water.

**Using solvents for Recycling**

A large amount of used lubricating oil from vehicles is produced each year which by increasing number of vehicles this producing is also increasing. As used lubricating oil partly contains water, salt, broken down additive components, varnish, gum and other materials and just a small part of this passes recovery process, it may leave the adverse impact on the environment [9, 10]. Due to this thought, employing an appropriate extraction technique to recycle used oil seems necessary. Recycling of oily sludge also has the same importance in environmental issues as the recovered oil can use for reprocessing, reformulating, or energy recovery [11-13]. Recycle of used oil has been carried out by several methods that among them solvent extraction has received considerable attention in recent years because it has a great tendency of solvent extraction to reduce sludge contaminants from 100 to 30% water and solid wastes and also in this technique the problem related to acid sludge produced from chemical treatment have been resolved [14]. Therefore, the
possibility of harmful effects of oil sludge on the environment with the recovery of recyclable hydrocarbons by exerting solvent extraction reduces which can improve the national economy [15]. Emam and Shoaib (2013) compared the solvent extraction/clay and acid/clay-percolation processes and concluded that the re-refined base oil using acid/clay percolation gave the best quality while using solvent extraction/clay treatment resulted in a higher yield of about 83%. The solvent that is chosen for this process should have some properties including having the maximum solubility for base oil and minimum for additives and carbonaceous matter. It had been shown that using propane and ethane as extracting solvents giving low yield 72-80% [16, 17]. Generally cheap and low boiling point solvent (such as methyl ethyl ketone) at the ambient temperature used in this process that at the end of process solvent could be recovered by distillation [18, 19]. However, a mixture of polar solvents (n-hexane, 2-propanol, 1-butanol) in presence of potassium hydroxide on waste oil sludge removal had been studied by Martins (1997). The results showed that 0.25 waste oil, 0.35 n-hexane, and 0.4 polar compounds (80% 2-propanol, and 20% 1-butanol with 3 gm/l KOH) is an economical aspect for the extraction–flocculation process in the re-refining of waste oils. Taiwo and Otolorin (2009) by using different solvents such as hexane, xylene, kerosene, and ethyl acetate for separation of the recyclable components from Petroleum reported that about 73.24% of volatile and non-volatile hydrocarbons were extracted from the sludge which hexane shows the highest performance in extracting useful hydrocarbon from the sludge. However comparing four solvents (hexane, xylene, ethyl acetate and kerosene) for extraction of petroleum hydrocarbon from sludge showed the highest extraction ability of hexane and the least extraction efficiency of kerosene (about 67.48% and 62.55% respectively;) [20]. Alves and Geronimo (1988) by using ketones and alcohols that are miscible with base oils at room temperature described that the flocculating mechanism of polar solvents in waste oils is related to an anti-solvent effect on some non-polar macromolecules, and sludge removal from waste oil by adding KOH in alcoholic solution increases.

**Use Solvent for Heavy Oil Recovery**

By depleting world’s crude oil resources, attention toward heavy oils and bitumen to supply the demand for fuels and petrochemical feedstock has increased [21-23]. Heavy oil or extra heavy crude oil could be definite as a type of crude oil which does not flow easily and its density or specific gravity is higher than light crude oil [24-26]. Many techniques have been employed to
achieve the economic recovery process in oil fields [27-29]. Using steam combined with appropriated hydrocarbon solvents was showed a most cost-efficient recovery process. As solvent extraction requires no water, the solvent is recoverable and reusable, and depending on the mode of operation, solvent extraction is a suitable alternative for all recovery methods. The basis of solvent extraction is injecting diluents like naphtha or light oil and some vaporized hydrocarbon solvent, usually, ethane, propane, or butane to the pump to reduce the viscosity of the heavy oil to make pumping easier [30, 31]. Vapor Extraction (VAPEX) and enhanced solvent extraction (N-Solv TM) methods are effective in reducing the bitumen’s viscosity as Marin (2015) reported inject a light hydrocarbon solvent into an upper horizontal well of the heavy oil, reduced the heavy oil viscosity and allowed it to drain under gravity to a bottom production well. Mitchell and Speight (1973) described that in the solvent process solvent extracts soluble components of heavy oil and solubilization of the asphaltic constituents occurs by initial contact between the solvent and the oil at a low solvent-to-oil ratio. However, that there are not the usual concerns over the solvents’ interactions with the reservoir minerals. It is known that clay adsorbs organic solvents very strongly, and it can also pollute underground formations such as aquifers [32, 33].

**Use of solvent to Reduce Crude Oil Viscosity**

Flow ability of crude oil for transportation through pipelines is an important factor and it depends on crude oil composition, density, viscosity, and ambient temperature conditions. The high viscosity of oil lead to large pressure drops increased pumping costs, blocked pipelines, and production loss. So many efforts performed to reduce heavy oil viscosity such as adding normal alkane liquids to oils. Viscosity reduction has become the common element of in-situ methods of heavy oil recovery with the exception of cold production. Since thermal methods require intensive energy and vast volumes of water, they aren’t beneficial treatments. Therefore solvent extraction with a desirable advantage like the solvent is recoverable and reusable is one alternative choice [26, 34].

Argillier et al (2001) reported that alcohols are more effective in reducing the viscosity. Hasan et al [2010] in their study showed that using 10% ethyl alcohol reduced the viscosity of crude oil about 80% at 250°C. Kulkarni and Wani (2016) related this result to the interaction between the hydroxyl groups and asphaltenes because of heavy oil (API < 20) and extra heavy oil (API < 10) have a high proportion of asphaltenes and paraffin [34]. Studies have indicated that some organic
solvents/distillates such as gasoline and kerosene because of their good solvent properties used as distillates widely. Yaghi and Benami (2002) indicated that 15% kerosene mixed with heavy oil at 50°C and 20% kerosene at room temperature achieves the same viscosity reduction. Comparing Methyl Tert-Butyl Ether (MTBE), Tert- Amyl Methyl Ether (TAME) and dimethyl ether (DME) showed that the recovery of DME is easier than other solvents. The nanotechnology has played an important role to introduce revolutionary changes to several areas of oil and gas industries such as exploration, production, enhanced oil recovery, and refining [35, 36]. For example, smart fluids are a new type of fluids that are created by adding nanoparticles to fluids for intensification and improvement of some properties at low volume concentrations of the dispersing medium. The properties of Nano fluids greatly depend on the dimensions of nanoparticles that are their components [35]. Increase in sedimentation stability, thermal, optical, stress–strain, electrical, rheological and magnetic properties are the main advantages of suspensions of Nano-dimensional particles which often exceed the properties of conventional fluids [36-38]. In oil and gas industry Nano fluids has found a great practical importance [39, 40], as solvent diffusion is used to further reduce the viscosity and produce the oil by gravity. Chen et al. (2009) by studying the viscosity reduction of nano-keggin-K3PMo12O40 showed that nano-keggin-K3PMo12O40 was changed in oxygen-containing groups during the catalytic aqua-thrombolysis. Also, the effect of Nano sized metal on the viscosity reduction of heavy oil/bitumen proved that Nano sized particles had a remarkable effect on heat transfer through heavy oil [41].

**Oil Recovery techniques**

Different Enhanced Oil Recovery (EOR) methods with varying degrees of success for the recovery of both light and heavy oils, as well as tar sands have been used in the past. These techniques are primary and secondary methods including thermal and non-thermal methods. The non-thermal involve methods chemical (flooding with chemicals) and the thermal methods include steam injection, hot water flooding, and sit combustions. The miscible method (mixing of oil with a solvent) has been proposed as an alternate method [42, 43]. Although thermal methods are primarily intended for heavy oils and tar sands, they are also can use for light oils in special cases. However non-thermal methods are normally used for light oils [44, 45]. Steam-based methods among thermal methods and miscible flooding among non-thermal methods have been more successful than others. However, the availability and cost of solvents

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limit the applicability of miscible flooding on a commercial scale. Although chemical methods have generally been uneconomic in the past, but they hold promise for the future. The CO2 floods among immiscible gas injection methods have been more beneficial than others for heavy oils [45]. Historically, acid clay process technology for treating used oils had been known as the most successful technology. Additionally, good quality lubrication stock is produced in this method. However, produces large volumes of petroleum-contaminated acid clay sludge. The high cost of managing this residue made the acid clay process technology uneconomic. On the other hand low-temperature distillation for treating used oils in most small-scale facilities because this technology although can reduce water, antifreeze, and solvents in the used oil, it is limited in its ability to reduce ash and other residues, seriously limiting product marketability. So the solvent extraction technology has the potential to produce oil products that are superior to those produced by the low-temperature distillation process currently in use [46].

In 1987 there was a renewed interest in chemical enhanced oil recovery because of diminished reserves and advances in surfactant and polymer technology. But recently, Al-Hadhrami and Blunt (2001) by proposing a model explained the wettability alteration encountered during thermal operations in fractured carbonate systems. They supposed desorption of oil-wet asphalting macromolecules from rock surfaces when the temperature was over a critical value. Thus, the water-wet surface was produced. This finding was similar to Hjelmeland and Larrondo (1986). Although this mechanism is not likely for siliceous surfaces, laboratory experience suggests asphaltenes adhere irreversibly and stable [47]. Generally For dissolving asphaltenes adsorbed on siliceous solids some strong organic-phase solvents, like hot pyridine, are needed [48, 49].

Water flooding is the oldest secondary recovery method that is based on pumping water through injection wells into the reservoir. The water is forced from injection wells through the rock pores, sweeping the oil ahead of it toward production wells. Over time, the percentage of water in produced fluids—the water cut—steadily increases. This is practical for light to medium crudes. Water flooding is the low cost of energy because water is usually readily available and inexpensive [50]. It can be applied to the thin reservoirs, with bottom water or reactive mineralogy, and it also has the potential for in situ upgrading. This process can apply for paired and single horizontal wells, or a combination of vertical and horizontal wells. Water flooding may increase the recovery efficiency to as much as
60% or more of the original oil in place. Kumar (2006) reported incremental recovery of approximately 2 to 20% of the original oil in place.

Desulfurization of petroleum fractions by solvent extraction

Petroleum oil composition is typically different from its origin or geographical location of the refinery [51, 52]. Crude oil is consisting of various individual fractions at different boiling points. The fractions with boiling above 350°C which termed as residues and are obtained after most of the distillable products have been removed from the petroleum oil [53, 54]. These residual petroleum oils are contain different amount of sulfur typically varying from about 1 – 4%. However, some of them may contain up to 6-8 % Sulfur [55]. In the other hand a large portion of sulfur compounds can be transferred to diesel oil during refining process as hydrogen sulfide, organic sulfides and disulfides, benzothiophene, dibenzothiophene, and their alkylated derivatives [56].

The adverse environmental and public health issues caused by sulfur emissions, leads to reducing sulfur content in fuels become an important priority in oil industry. More recently, by proving adverse effect of fuel sulfur on particulate emissions from diesel engines [57-60], new legislation in Europe and the US was executed in which the maximum allowable sulfur content in gasoline and diesel fuels limits to 0.05% maximum [61, 62]. The conversion of sulfur into sulfur oxides (Sox) that during combustion in the engine occurs along with Oxides of Nitrogen (NOx) gets adsorbed by the water molecules in the atmosphere resulting in acid rains. Besides, sulfur is also harmful to modern vehicles more sensitive to the quality and purity of fuel. As the efficiency and lifetime of emission gas treatment systems in cars with a higher concentration of sulfur in fuels significantly decreases [63-65].

Various chemical processes with indifferent success for removing sulfur were tried in the past [66], including catalytic transformation processes such as hydro-desulfurization [67-69] and physio-chemical processes such as solvent extraction [70, 71], oxidation [72-75], adsorption [76-78], sodium metal reduction [79, 80], bio-enzymatic [81, 82], electrochemical [83-85] etc. As hydro desulfurization requires the high reaction temperature and pressure, large reactor volumes and highly active catalysts Oxidational Desulfurization (ODS) can be an economical alternative to lower the sulfur content of diesel fuel [86-88]. In the oxidants oxidize organic sulfur and the reaction products are removed by liquid extraction or adsorption. The most efficient and available
extractive agent is an aqueous solution of acetone. However, a wide variety of polar solvents and binary systems, namely methanol, N, N-dimethylformamide, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile can be used in this process [89-92]. In desulfurization by solvent extraction the organic sulfur compounds are removed from the solvent by distillation and the solvent is recycled. The solubility of the organic sulfur compounds in the applied solvent, it is very important factor of extractive desulfurization efficiency, hence choosing the proper solvent according to the nature of the present organic sulfur compounds is also important [88, 93-95]. It was observed that when hydrogen fluoride was used as the extraction solvent, extremely high selectivity could be attained in the removal of sulfur compounds from middle distillate fractions [96].

Sulfolane and ionic liquids are solution which is exclusively used as solvent in the industry. Sulfolane with commercial name of 2, 3, 4, 5-tetrahydrothiophene-1, 1-dioxide, is an organic sulfur with high solubility in water, have the ability to extraction polar sulfur compounds and aromatics from hydrocarbon mixtures. AdPamiaé et al (2007, 2010) have reported the removal efficiencies of from FCC gasoline with sulfolane up to 89% of total sulfur content. Ionic liquids are solutions made up of ions which are mostly fluids at room temperature. These ionic liquids are capable of removing organic sulfur compounds without removing aromatics at the same time, which is desirable because when the feed is gasoline this does not cause the reduction in octane number [97]. However, the overview of desulfurization with different types of ionic liquids, particularly the most promising water-stable and less costly 1-n-butyl-3-methyl-imidazolium-octylsulphate by Eåer et al (2004) indicated that nitrogen compounds are found to be more efficiently extracted than sulfur compounds. This problem is mainly associated to efficiency of a limited number of organic sulfur compounds for particular ionic liquid, cross-solubility of hydrocarbons, and the regeneration of expensive ionic liquid compounds [97-99]. With regard to difficulties associated with ionic liquid such as involving several synthetic steps that often result in by-products and waste generation, the toxicity, poor biodegradability and the high cost related to the synthesis [100-102], the industrial applications of ionic liquid has limited. Therefore, the concept of ‘greenness’ particularly, sustainable/green solvents has been developed. In 2003, a new generation of sustainable solvents was discovered, so-called deep eutectic solvents [103-105]. DESs as the future green solvents in many applications are suitable alternatives of ionic liquids.
with similar properties (i.e. low vapor pressure, wide liquid range, thermal stability, and low flammability) without some defects of them. Meanwhile, the DESs proved to have much higher selectivity than sulfolane which is the commercially used solvent [102]. However, ionic liquids can be prepared in high purity, simply by mixing low-cost hydrogen bond donor (HBD) and at least one hydrogen bond acceptor (HBA) compounds that are mostly naturally occurring and can be biodegradable. Some applications of DESs are in separation processes of oil and such as: DE aromatization, desulfurization, the removal of glycerol from biofuel and natural gas sweetening [102]. An excellent extraction performance of different aromatic compounds from aliphatic hydrocarbons by DESs has been demonstrated [106-112]. Although commonly solvents like sulfolane and ethylene glycol are used as extractants for DE aromatization [113], but they are volatile, toxic and flammable, therefore DESs can be suitable replacements with some benefits such as reduce energy consumption, allow the use of alternative solvents and renewable natural products, and ensure a safe and high-quality extract/product [114]. Recently deep extractive desulfurization of fuels for removal sulfur-containing aromatics such as thiophenes from fuels by using green carboxylic acid based DESs has been performed [115] and excellent efficiency of this process with a possibility of regeneration of the DESs (using methyl Tert-butyl ether as back-extractant, [102]) have been reported [94, 116-119]. However using DESs in the oil purification in order to remove glycerol from biofuels and extraction of different aromatic compounds from aliphatic hydrocarbons are another application of these solvents [106-112, 120].

**Using solvent to recovery of metal values from spent petroleum**

By the gradual depletion of Mo and V containing ores and also increasing demand, attention toward alternative resources include secondary sources such as spent petroleum catalyst has been raised [121, 122]. The spent petroleum catalyst from petroleum industry have shown to contain metals such as Mo, V, Ni, Co, Al, S etc., in different concentration depending on the nature of catalyst and crude oil [123-125]. Various methods to recover metal values from waste petroleum catalyst have been proposed [125, 126-138]. However, the combination of acid leaching followed by solvent extraction route is an appropriate route to recover selectively the metal values from spent petroleum catalyst. As more than 95% recovery of V, Ni and Fe in a single stage within 1 h of reaction period by acid leaching (1 M H2SO4) have been shown [122, 139, 140].
Conclusion
Due to the importance of petroleum resources as a major incoming source word-wild and increasing production costs, finding a method with higher efficiency are taken into consideration. This also includes recycling hydrocarbons using sustainable methods. Solvent extraction as an efficient method causes higher oil production compared to other thermal and non-thermal technique. Knowing about diluents properties to achieve the desired crude and heavy oil viscosity reduction is the main object of this review.

Reference

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