DEEP CONVERSION OF RESIDUES
Deasphalting

7.1.1 Introduction

Crude oil contains hydrocarbons covering a very wide boiling range. It is normally separated into various fractions, which are further processed to produce marketable products.

The lower boiling fractions are usually separated and recovered in an atmospheric distillation column. Since heavier petroleum fractions are subject to thermal degradation, there is a limit to how much material can be recovered in this column.

Additional distillates are generally recovered in a vacuum distillation column. More material can be recovered without thermal degradation by increasing the vacuum.

Even after vacuum distillation, there are still hydrocarbons left in the vacuum residuum, suitable for upgrading to valuable products.

Solvent deasphalting permits recovery of non-asphaltic material, either directly from atmospheric residuum or, more frequently, from vacuum residuum.

In the former case, vacuum distillation unit is not needed. Solvent deasphalting achieves higher recoveries at relatively low operating temperatures. Low molecular weight paraffins, propane ($C_3$) to pentane ($C_5$), are normally used as the solvent.

The deasphalting process separates hydrocarbons according to their solubility in the solvent. Therefore, paraffinic and lower molecular weight material is preferentially extracted as DeAsphalted Oil (DAO), and the heavier and more aromatic material is rejected into the asphaltic raffinate.

7.1.2 Evolution of deasphalting

Solvent deasphalting was originally developed as a joint effort of Standard Oil Company of New Jersey, Standard Oil Company of Indiana, Union Oil Company of California and M.W. Kellogg Company (Chang and Murphy, 1992).

The objective of their combined research efforts was the recovery of heavy lubricating oils (known as bright stocks or cylinder stocks) from asphalt-base crude oils. Since these heavy lubes could not be readily distilled without thermal degradation, they were available only from the paraffin-base crude oils containing little or no asphalt. Only from these crudes, the heavy fractions could be economically recovered by steam or clay refining.

The separation of residual fractions from asphalt-base crudes into oil and asphalt fractions was first performed on a production scale by mixing the residue of vacuum distillation with propane and continuously decanting the resulting phases. The temperature was maintained within about 40°C of the critical temperature of the solvent to regulate the yield and properties of the deasphalted oil and to reject the undesirable components as asphalt.

From this original process, pilot plant development progressed through multi-stage countercurrent designs. The multistage settlers were later replaced by a countercurrent extraction column. Fig. 1 presents a simplified flow diagram for a conventional deasphalting unit.

Recovery of the solvent from the DAO is the major capital and operating expense. Most of the older units used a single stage of evaporation and consumed large amounts of energy, primarily
steam. As energy grew more expensive, the energy efficiency of the solvent deasphalting units was increased through the use of double-effect evaporators. Kerr-McGee Corporation took the energy efficiency a step further when it developed the ROSE (Residuum Oil Supercritical Extraction) process. This system operated in the supercritical region of the solvent; over 90% of the solvent can be recovered in the supercritical region, thus the heat of vaporization is essentially eliminated. Supercritical process is the method of choice for new solvent deasphalting units. This made the solvent deasphalting process much more energy efficient than not only older solvent deasphalting units, but also vacuum distillation processes, both of which require evaporation and condensation.

**Fig. 2** provides a simplified flow diagram for a ROSE unit utilizing supercritical solvent recovery. In addition, **Fig. 3** shows how a conventional deasphalting unit can be ‘converted’ to supercritical solvent recovery.

### 7.1.3 Basic principles of solvent deasphalting

Similar to atmospheric and vacuum distillations, solvent deasphalting is a separation process that does not perform chemical conversion of the feedstock. Unlike the distillation processes, however, deasphalting does not rely on boiling point differences to achieve the separation. Instead, it depends on solubility differences. The solvent is low-molecular-weight paraffin and dissolves lower molecular weight material and paraffinic material. The degree of solubility in the solvent, and thus the amount of material separated from the residuum, can be controlled by changing the molecular weight of the solvent. The lower molecular weight solvent (e.g. propane) will separate lower boiling material rather than a heavier solvent (e.g. pentanes).

Propane is the lowest molecular weight solvent that is typically used in deasphalting. As such, it dissolves less of the vacuum residue than any of the heavier solvents. The separated oil is low in contaminants such as metals, carbon residue, nitrogen, etc., and is normally a good lubricating oil-base stock.

Higher boiling point paraffins are used when deeper deasphalting is desired. More and more material can be dissolved as the solvent boiling point, or molecular weight, is increased. Custom solvents for different applications can be prepared by blending C$_3$, C$_4$, C$_5$ and C$_6$ paraffins. The ability to control the quantity of the material separated (i.e. DAO) and the quality of this material makes solvent deasphalting particularly suitable for integration with downstream units. The quality of the desired DAO is used in selecting...
solvent for the application. As the quantity of DAO increases, its quality generally decreases; its aromatic content increases as does the quantity of impurities such as sulphur, nitrogen and metals.

7.1.4 Deasphalting processes

Commercial deasphalting units that produce lubricating oil stock existed before the Second World War. The basic principles of these units
have remained essentially unchanged; however, hardware and energy efficiency have improved dramatically. One important energy improvement was the introduction of the double-effect evaporation scheme. In this system, part of the solvent in the DAO is evaporated at high pressure and separated from the liquid. The liquid is let down in pressure to decrease its boiling point below the condensing temperature of the high pressure solvent vapour. The two streams are then sent to a heat exchanger, where the heat of condensation of the high pressure vapour is used to vaporize most of the remaining solvent in the DAO. Even greater efficiency was achieved with a triple-effect evaporation system. The major energy efficiency breakthrough was the introduction of the supercritical solvent system (see below).

**Conventional versus supercritical solvent recovery**

The supercritical solvent recovery technique saves significant energy because only sensible heat is required to raise the operating temperature to supercritical conditions. In conventional technology, both sensible heat and latent heat are required to vaporize the solvent. By avoiding solvent phase change, energy usage for the solvent separation in supercritical solvent deasphalting is less than half of that for a conventional solvent deasphalting unit. The overall energy savings also depend on the level of heat integration used in the conventional process. Approximate relative energy costs are given in Table 1.

The advantages of supercritical solvent recovery on the overall utility requirements can be illustrated by means of the typical solvent pressure-enthalpy phase diagrams. Fig. 4 illustrates the energy requirements to recover the solvent in the DAO for a conventional recovery system. All of the solvent used to extract the DAO leaves the extraction column as a liquid at a relatively low temperature and high pressure (point A). This solvent plus DAO stream is heated and flashed to some point, E, in the vapour region of the solvent’s enthalpy diagram. At E, virtually all of the extraction solvent is vaporized, leaving a small amount of solvent to be stripped. This remaining solvent is stripped with steam at a higher temperature and a much lower pressure (point F).

With supercritical solvent recovery (Fig. 5), the extraction solvent and DAO begin at approximately the same temperature and pressure used in the conventional case (point A). However, in a supercritical unit, the DAO plus the solvent stream is heated by cross-exchange with supercritical solvent to an elevated temperature (point B). The DAO plus the solvent stream is then heated by hot oil heat exchange (or, in some cases, high pressure steam or direct-fired furnace) to a supercritical temperature, point C, prior to entering the supercritical separator. At the supercritical conditions maintained in the separator, a phase separation occurs with as much as 85-93% of the solvent being recovered as a supercritical fluid. The supercritical solvent, containing virtually no entrained/dissolved DAO, is then circulated back through a set of cross-exchangers where much of its heat is transferred to the DAO plus the solvent stream (point D). The solvent is then cooled enough to maintain the desired extraction temperature and pumped back to the extraction column, thus completing the loop. The residual solvent dissolved in both the DAO and asphaltene products is recovered by

<table>
<thead>
<tr>
<th>SOLVENT RECOVERY TECHNIQUE</th>
<th>RELATIVE ENERGY COST</th>
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<tr>
<td>Single-effect evaporation</td>
<td>280</td>
</tr>
<tr>
<td>Double-effect evaporation</td>
<td>170</td>
</tr>
<tr>
<td>Triple-effect evaporation</td>
<td>150</td>
</tr>
<tr>
<td>Supercritical unit</td>
<td>100</td>
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</tbody>
</table>

**Table 1. Relative energy costs of solvent recovery techniques**

![Fig. 4. Conventional solvent recovery: solvent Mollier diagram.](image)
flashing and stripping, similar to a conventional solvent deasphalting process (points E and F). However, only 7-15% of the extraction solvent must be heated to E for recovery compared with 100% of the solvent in the conventional case. The actual quantity of dissolved solvent in the products, on a standard volume basis, depends on the solvent composition and operating conditions within the extraction column and the supercritical separator, and ranges from 0.9 for propane to 0.6 for pentane.

The enthalpy diagrams clearly demonstrate the energy efficiency of heating from point A to point C with a supercritical system as opposed to heating from point A to point E by conventional methods. Heat integration further reduces the enthalpy requirements as demonstrated by the actual heat input required for heating from point B to point C.

7.1.5 Operating variables

Solvent deasphalting has three main operating variables: solvent type, solvent/oil ratio, and extraction operating temperature.

Solvent type

As discussed earlier, the heavier the solvent, the higher the maximum yield of DAO. However, the higher density and molecular weight of the heavier solvent also results in extraction of some of the heavier oils and resins from the feedstock. Therefore, the DAO quality deteriorates at the higher yield. All impurities increase with an increase in the DAO yield. For example, Fig. 6 shows how the DAO sulphur concentration increases as the DAO yield increases.

In general, the solvent should be selected to maximize the DAO yield while meeting all DAO quality specifications. The DAO product is most often used in the production of either fuels (gasoline or diesel) or lube bright stocks. Propane solvent is generally used for production of lube bright stock, butane for hydrotreating or hydrocracking, and pentanes for fluid catalytic cracking services. To achieve optimum DAO yield sometimes a solvent comprising a mixture of C₃, C₄, and C₅ paraffins is used. In the few cases where DAO is intended for blending into fuel oils, heavy C₅ and C₆ solvents can be used.

Using a mixed solvent offers at least two benefits to the refiner: first, the solvent can be optimized to maximize the DAO yield; second, the deasphalting solvent can be obtained from other refinery units without splitting the stream into ‘pure’ solvent components. Periodic samples of the circulating solvent need to be checked to ensure that the solvent composition stays within operating targets. By preferentially removing the heavier component of fresh solvent with the products, the quality of the circulating solvent can be adjusted.

The type of solvent used also affects the process flow scheme. Propane (and, in some
cases, i-butane), due to its higher volatility, can require a compressor system for the overhead from the low-pressure stripper as well as a high-pressure flash drum. This solvent recovery equipment (i.e. compressor and high-pressure flash drum) is not required with the heavier solvents.

**Solvent/oil ratio**

The solvent to oil (S/O) ratio is defined as the ratio of the volume of solvent to the volume of residuum feedstock at 60°F (16°C) entering the extraction column. The selected S/O ratio is an optimization between the benefits of DAO yield and/or improvements, operating stability, the costs of utilities and equipment size. The normal range of solvent/oil ratio for a ROSE unit is between 5 and 8.

At higher S/O ratios, the density difference between solvent plus DAO and asphaltenes is greater. As a result, the separation of asphaltenes from solvent plus DAO is easier, and finer separation between solvent/DAO and asphaltenes can be obtained. This reduces the chance of asphaltene carryover with solvent/DAO stream during minor upsets. Therefore, the allowable solvent superficial velocities are greater and may result in a lower diameter and length of the separation tower. Moreover, the concentration gradient and the mass transfer coefficient between the residuum feedstock and the bulk solvent are greater, thus resulting in improved mass transfer rate. Consequently, the higher S/O ratios result in higher DAO yields at constant quality or improved quality at constant yields.

**Extracting operating temperature and use of internal reflux**

The operating temperature in the asphaltene separator impacts the overall yields and qualities of the extracted products because of the effect of temperature on the solubility of the feedstock constituents. The solubility of DAO in solvent is directly proportional to the density of solvent. Therefore, DAO yield can be optimized by adjusting the temperature of the separator(s). It must be emphasized that temperature also impacts the quality of DAO extracted. Pressure has much less impact on solvent density and therefore does not provide the same degree of control as temperature.

An additional method to improve the DAO quality is to use a set of heating coils located in the top section of the separator column.

This generates an internal reflux, which reduces the concentration of asphaltene material with solvent/DAO stream. This also reduces Conradson Carbon Residue (CCR), metals content, and improves the color of the DAO product. The use of internal reflux also reduces the allowable fluid velocity within the separator and hence requires a larger diameter separator. Internal reflux is usually used when very clean DAO is required, such as in the production of lube bright stocks and cylinder oils.

**Product yield and qualities**

The data shown in Table 2 are ‘typical’ for a Middle Eastern vacuum residue for four different solvent compositions at an 8:1 S/O. The maximum DAO yield is obtained by using n-pentane, the heaviest solvent tested. As lighter solvents are used, solvency is reduced and the maximum DAO yield decreases.

The maximum DAO yield for a given solvent composition is the point beyond which reducing the separator temperature has no noticeable impact on DAO yield. With a constant solvent composition, the DAO yield can be reduced by increasing the extraction temperature; this DAO yield and quality relationship is referred to as an operating curve.

### 7.1.6 Product uses

DAO and asphaltene are not finished products and require further processing for the production of end products.

**DAO**

**Hydroprocessing**

The DAO is hydrotreated or hydrocracked in conventional fixed bed hydrotreaters, usually along with gas oils. The hydrotreated DAO can then be converted into gasoline in FCCU (Fluid Catalytic Cracking Units).

<table>
<thead>
<tr>
<th>Table 2. Maximum DAO yields</th>
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<tr>
<td><strong>SOLVENT COMPOSITION</strong></td>
</tr>
<tr>
<td>n-pentane</td>
</tr>
<tr>
<td>n-butane</td>
</tr>
<tr>
<td>i-butane</td>
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<tr>
<td>propane</td>
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Good quality distillate products are produced by hydrocracking. Another option is to partially convert DAO to distillate in a hydrocracker followed by cracking an unconverted portion of DAO in the fluid catalytic cracking unit to obtain a mix of gasoline and distillate products.

**Direct cracking in FCCU**

The DAO, usually along with gas oil, is sent directly to the FCCU to produce gasoline. For the maximum-gasoline case, however, the FCCU products will need to be hydrotreated to meet product specifications. In addition, the FCCU flue gas will need to be desulphurized to meet environmental requirements.

**DAO to lubricating oil**

Some refineries make lubricating oil from the DAO. These deasphalting units use propane as the solvent and do not produce large quantities of DAO. This DAO is further treated (normally with furfural) to remove aromatics and then dewaxed to produce lubricating oil stocks. Mild hydrocracking may also be used to make the lubricating oil-base stocks.

**Asphaltene**

**Asphaltene product to fuel oil**

It is sometimes possible to burn the asphaltene product directly as fuel oil. In most cases, it is first blended with other low-value streams to produce a lower viscosity product that meets fuel oil specifications. The fuel oil production can often be cut to less than half by blending asphaltene instead of vacuum residuum into fuel oil. Asphaltene quality depends on crude. As the crude slate becomes heavier and more sour, the asphaltene produced from these crude oils will also contain a higher quantity of contaminants. Environmental regulations will therefore dictate how much flue gas cleanup is required and, hence, the viability of direct firing burning of asphaltenes.

Some refiners blend the asphaltene with distillate materials to produce No. 6 fuel oil. Distillate from the FCCU makes excellent blending stock because of its high aromatic content. A visbreaker can be used to reduce the viscosity of the asphaltene and thus reduce the required amount of blending stock. However, the high sulphur content of the asphaltene may limit its use in No. 6 fuel oil production.

**Commercial asphaltenes**

Specialty products, such as paving asphaltene or roofing asphaltene, can be made by blending the solvent asphalt with suitable aromatic oils.

It is possible to have a three-step deasphalting unit that produces DAO, asphaltenes and an intermediate product, normally called resins. This third product greatly increases the blending flexibility to produce specialty products.

**Asphaltene coking**

Refiners are now successfully cracking asphaltenes in their cokers. Normally asphaltene is blended with vacuum residuum to achieve good flow properties. The blend is then cracked in cokers. Asphaltene cracking is being carried out by both delayed and fluid coker operators. Cracking ROSE asphaltene instead of vacuum residuum reduces total coke make by 10-20%. The liquid yield also improves.

**Asphaltene to partial oxidation unit**

The asphaltene can be fed to a partial oxidation unit to produce synthesis gas. Hydrogen in the synthesis gas can be used for hydrossociating units. The remaining synthesis gas is fired to produce steam and power.

**Solid fuel**

There are existing commercial technologies to produce solid fuel from the solvent asphaltene. However, these processes are generally high in maintenance, low in reliability and are manpower intensive. The new AQUAFORM process offered by Kellogg, Brown & Root produces solid pellets that are stable, can be stored and are easily transportable. The pellets have high heating value and low attrition rates. The solid fuel produced from heavy and sour oils will be high in sulphur. Therefore, it can be used only in boilers with stack-gas cleanup or in fluidized-bed boilers that use limestone to capture sulphur oxides from the combustion products. The potential users of these pellets are cement, steel, partial oxidation units (gasifiers), cokers, and utility companies.

**Bibliography**


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References


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