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New approaches to hydroprocessing

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Abstract

Heavy oil conversion adds a new dimension to refinery operations that requires the use of units to prevent high yields of coke and more beneficial yields of distillate products. Typically, heavy oil conversion involves two general routes: (1) carbon (coke) removal as a product having a low atomic hydrogen/carbon ratio and, at the same time, to produce overhead material (distillate) having a high atomic hydrogen/carbon ratio; and (2) hydrogen addition by a hydrocracking/hydrogenolysis mechanism by which the yield of coke is reduced in favor of enhanced yields of liquid products.

Efficient conversion of heavy oil by fluid catalytic cracking or by hydrotreating requires serous efforts to develop adequate catalysts as well as the modification of existing, or the development of new, processes. The constituents of heavy oil are deleterious to catalyst activity and to on-stream lifetime and there is the need to develop catalysts that are tolerant to the high molecular weight and metal constituents of the feedstocks.

Alternative processes include hydrotreating coupled with coking or visbreaking. Such options combine the benefits of higher liquid yields from hydrogen addition with the benefit of the added hydrogen during the thermal process. Furthermore, hydrovisbreaking is receiving some attention as a possible alternate to visbreaking and coking. Hydrovisbreaking heavy oil and thermal cracking (e.g., coking, fluid catalytic cracking) the liquid product process (coking) offers the potential for higher yields of distillate with corresponding decreases in the yield of coke. Further development of these and process other concepts are needed to enhance the conversion of heavy oils.

Keywords: Hydroprocessing; Catalyst; Hydrotreating

1. Introduction

Heavy oil refining adds a new dimension to refinery operations that requires the use of units to prevent high yields of coke and more beneficial yields of distillate products. Typically, one-third or more of the heavy oil barrel is residuum, or material boiling above (565 °C) 1050 °F. In addition, the chemical composition of heavy oil is complex [1–4]. Physical methods of fractionation indicate high proportions of asphaltenes and resins, even in amounts up to 50% (or higher). In addition, the presence of ash-forming metallic constituents, including such organometallic compounds as those of vanadium and nickel, is also a distinguishing feature of the extra heavy oils.

The properties of heavy oil can be summarized quite conveniently. This type of feedstock (1) is usually non-volatile below 200 °C (390 °F), (2) has an API gravity less than 20° and a high viscosity, (3) contains high proportions of asphaltenes and resins, (4) contains high proportions of sulfur (often more than 2%, w/w) as organically bound sulfur, and (5) contains high proportions of metallic ash-forming constituents (several thousand part per million).

2. Upgrading heavy oil: process types and process design

Typically, heavy oil conversion is often achieved directly by using the heavy oil as feedstock or indirectly by using the residuum as feedstock and involves two general routes: (1) carbon (coke) removal as a product having a low atomic hydrogen/carbon ratio and, at the same time, to produce overhead material (distillate) having a high atomic hydrogen/carbon ratio; and (2) hydrogen addition by a hydrocracking/hydrogenolysis mechanism by which the yield of coke is reduced in favor of enhanced yields of liquid products.

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Thermal conversion does not require the addition of a catalyst; therefore, this approach is the oldest technology available for heavy oil/residua conversion. Examples of the carbon rejection processes are thermal cracking, visbreaking and the coking processes whereas examples of the hydrogen addition concept are found among the various hydrocracking processes [2,3,5,6]. However, coke yield may be in excess of 20% (w/w) of the heavy oil feedstock and contains the majority of the sulfur, nitrogen and metals originally in the heavy oil.

2.1. Thermal cracking processes

The majority of thermal cracking processes use temperatures of 455–540 °C (850–1005 °F) and pressures of 100–1000 psi.

The older Dubbs process employed the concept of recycling in which the gas oil was combined with fresh feedstock for further cracking. Cracked gasoline and middle distillate fractions are removed from the upper section of the column. Light and heavy distillate fractions are removed from the lower section of the column. Higher temperatures are used to crack the more refractory light distillate fraction. The streams from the heaters are combined and sent to a soaking chamber, where additional time is provided to complete the cracking reactions.

Mild cracking conditions (a low conversion per cycle) favor a high yield of gasoline components with low gas and coke production, but the gasoline quality is not high, whereas more severe conditions give increased gas and coke production and reduced gasoline yield (but of higher quality). With limited conversion per cycle, the feedstock needed to be recycled. However, the recycled feedstock becomes increasingly refractory upon repeated cracking and, if not required as a fuel oil stock, may be subjected to a coking operation to increase gasoline yield or refined by means of a hydrogen process.

2.1.1. Visbreaking (thermal viscosity reduction)

Visbreaking uses the approach of mild thermal cracking as a relatively low severity approach to improve the viscosity characteristics of heavy oil without attempting significant conversion to distillates. Low residence times are required to avoid coking reactions [3,6], although additives can help to suppress coke deposits on the tubes of the furnace.

The visbreaking process consists of a reaction furnace followed by quenching with recycled oil. The product mixture is then fractionated. All of the reaction in this process occurs as the oil flows through the tubes of the reaction furnace. The severity is controlled by the flow rate through the furnace and the temperature. Typical conditions are 470–500 °C (880–930 °F) (at the furnace exit with a residence time of 1–3 min). Many visbreaker units can operate for 3–6 months before the furnace tubes must be decoked [5]. Attempts to increase conversion of heavy oil during visbreaking will bring on sediment deposition.

2.1.2. Coking processes

Coking processes have the virtue of eliminating the residue fraction of the heavy oil feedstocks, at the cost of forming a solid carbonaceous product. The yield of coke in a given coking process tends to be proportional to the carbon residue content of the feed (measured as the carbon residue of the feedstock [3]).

Delayed coking is widely used for heavy oil conversion to distillates but coke disposal is necessary through sales or as fuel. The process operates in a semi-batch mode in which the heavy oil feedstock is heated to ca. 500 °C (930 °F) after which it is accumulated in one of a pair of coke drums. The vapor products, consisting of gases and distillates, are drawn off the top of coke drum (at ca. 435 °C; 805 °F) and coke accumulates in the drum. When the drum is full, the products are switched to a companion coke drum and the coke product is recovered from the first drum, usually by use of high-pressure water. When the second drum is filled with coke, the operation is switched to the now-empty first drum. A typical cycle spans 48 h.

Fluid coking (fluidized-bed coking, or fluid bed coking) is a continuous process in which the heated heavy oil is sprayed into a fluid bed of coke particles. Coking occurs on the surface of these particles at temperatures of 510–520 °C (950–970 °F). The cracked vapors rise to the top of the reactor where they are quenched by contact with condensed liquid or fresh feed. The heat to drive the cracking reactions is provided by burning a portion of the coke to heat the remaining solids. The temperature of the fluid bed and the residence time of the feedstock constituents in the bed determine the product yields. The use of a fluidized bed reduces the residence time of the vapor phase products and reduces the yield of coke with a concomitant increase in the yield of gas oil and olefins.

Flexicoking is an alternate approach to fluid coking and uses a coke gasifier to convert excess coke to a mixture of carbon monoxide (CO), carbon dioxide and hydrogen (H_2). This can be achieved through the installation of a flexicoking unit. In this process, the coke is converted to a low-heating value gas in a fluid bed gasifier with steam and air. The air is supplied to the gasifier to maintain temperatures of 830–1000 °C (1525–1830 °F), but is insufficient to burn all of the coke.

2.1.3. Fluid catalytic cracking

Fluid catalytic cracking (FCC) processes are usually used for the cracking of petroleum gas oil and other heavy feedstocks resulting in a broad spectrum of a products ranging from hydrogen, C_1–C_4, higher hydrocarbons, to polymeric material adhering to the catalysts as coke. In catalytic cracking processes, high conversions are desired with minimum coke formation and catalyst poisoning.

Fluid catalytic cracking processes maintain catalyst activity at a high level by operating the reactor at a lowest temperature possible and designing the reactor for a maximum interaction between the catalyst and the reactive fluid [7,8].

2.2. Hydroprocesses

Hydroprocessing (i.e., hydrotreating and hydrocracking) technologies are mature technologies but still offer opportunities for heavy oil refining. New catalysts and process variations continue to emerge to meet the evolving needs of the refining industry. Both hydrotreating and hydrocracking offer some relief to increased coke yields but it must be recognized, at the expense of increased hydrogen costs. Process parameters may require hydrogen pressures of the order of 1500–2500 psi or even higher at temperatures in the range 370–425 °C (700–800 °F). Reactions are often slow requiring residence times of 2–4 h and the units require thick (10–12 in.) thick walls.

2.3. Chemistry

In many cases with heavy oil feedstocks, the removal of nitrogen is important, particularly when the higher boiling fractions are to be used as feedstocks for fluid catalytic cracking or hydrocracking. If not removed, coke formation is enhanced and the catalyst system deactivates due to coke deposition and catalyst poisoning. The nickel and vanadium constituents of the feedstock are the most abundant metals and, when deposited on the catalyst, fill up the catalyst pore system and blocking active sites.

The initial reactions in the coking of petroleum feedstocks that contain asphaltenes involve the thermolysis of asphaltene aromatic-alkyl systems to produce volatile species (paraffins and olefins) and non-volatile species (aromatics) leading to a relationship between asphaltenes content and carbon residue formation [9–11]. In addition, the formation of liquid hydrocarbon products creates region of instability causing the highly aromatic and highly polar (refractory) products separate from the surrounding oil medium as an insoluble phase and proceed to form coke.

Thermal studies using model compounds confirm that volatility of the fragments is a major influence in carbon residue formation and a pendant-core model for the high molecular weight constituents of petroleum has been proposed [12]. In such a model, the scission of alkyl side chains occurs thereby leaving a polar core of reduced volatility and leads to the formation of a carbon residue [12–14]. In addition, even one-ring aromatic cores can produce a carbon residue if multiple bonds need to be broken before a core can volatilize [12].

Nitrogen species also appear to contribute to the pattern of the thermolysis. For example, the hydrogen or carbon–carbon bonds adjacent to ring nitrogen undergo thermolysis quite readily, as if promoted by the presence of the nitrogen atom [9,15]. If it can be assumed that heterocyclic nitrogen plays a similar role in the thermolysis of asphaltenes, the initial reactions therefore involve thermolysis of aromatic-alkyl bonds that are enhanced by the presence of heterocyclic nitrogen. An ensuing series of secondary reactions, such as aromatization of naphthenic species and condensation of the aromatic ring systems, then leads to the production of coke. Thus, the initial step in the formation of coke from asphaltenes is the formation of volatile hydrocarbon fragments and non-volatile heteroatom-containing systems.

It has been reported that as the temperature of an asphaltene solution is raised from 100 °C (212 °F) to 400 °C (750 °F), there is a progressive decrease in the size of the asphaltene particles [16]. Furthermore, there is also the inference that the structural integrity of the asphaltene particle is compromised and that irreversible thermochemistry has occurred. Indeed, that is precisely what is predicted and expected from the thermal chemistry of asphaltenes and molecular weight studies of asphaltenes [3,17].

It is also interesting to note that although the aromaticity of the asphaltenes is approximately equivalent to the yield of thermal coke, not all the original aromatic carbon in the asphaltenes forms coke. Volatile aromatic species are eliminated during thermal decomposition, and it must be assumed that some of the original aliphatic carbon plays a role in coke formation. The process can be represented as involving a multi-reaction sequence [9]. Little has been acknowledged here of the role of low-molecular-weight polar species (resins) in coke formation. However, it is worthy of note that the resins are presumed to be lower molecular weight analogs of the asphaltenes. This being the case, similar reaction pathways may apply.

2.4. Compatibility

Coke formation is an important phenomenon during heavy oil processing and is a complex process ([3] and references cited therein) that involves feedstock chemistry and thermodynamics (i.e., phase separation of the coke precursors [13,18–28]).

Formation of coke (solids) was reported to be a function of the solvent characteristics [29]. As an example, it is known that resins provide a better environment for asphaltene constituents to remain in the liquid phase than that of the paraffinic solvents [30,31]. As the oil fraction and resin fraction of the feedstock is hydrocracked, the solubility of reacted and unreacted asphaltene constituents is reduced. Phase separation occurs and coke formation ensues ([12] and references cited therein).

3. Reaction kinetics and reactor design

Efficient operation of heavy oil upgrading processes involves knowledge of the simultaneous mass and energy transfer coupled with knowledge of the complex chemical reactions in multiphase flow systems. A comprehensive knowledge of fluid dynamics and chemical reaction rates are essential elements in heavy oil upgrading processes.

Fluid dynamics is related to the reactor type (fixed bed, fluid bed, ebullated bed, entrained flow, batch, back mixed tubular, etc.) which is important for the rate of mass and energy transfer between and/or within the phases, chemical kinetics are important for the reactor size (LHSV), reactor dynamics (i.e., control mechanism), product yield and quality [32]. Mechanism of the catalytic reactions (chemisorption, diffusion in porous media and catalytic reactions) and phase equilibrium (thermodynamics) relations are also important elements of upgrading processes [33].

Reaction rate measurements are generally performed using an isothermal batch reactor (involves differential equations) or a continuous stirred tank reactor (CSTR, involves algebraic equations). Experimental data are correlated using lumped species based on the boiling points, solubility or functional groups [34–36]. It is also possible to correlate the experimental data using the theory of reactions in continuous mixtures [37,38]. In chemical reactions involving fluids and particles (catalytic or non-catalytic), as reaction temperature increases, the overall process is shifted gradually from a kinetically controlled reaction to an intra-particle particle diffusion controlled reaction and thence to a fluid-particle external surface mass transfer controlled reaction [39,40].

4. Catalysts and catalyst development

The catalyst system, as loaded into the reactors of a heavy oil hydrotreating unit, is generally composed of a number of different types of catalysts which are designed for the specific process objectives, e.g., hydrodesulfurization, hydrometallization, hydrodenitrogenation and mild hydrocracking. The high concentrations of heteroatoms (sulfur and nickel), metals (nickel, vanadium and iron) and coke precursors typically found in heavy oil have a major influence upon catalyst performance and must, therefore, be considered in catalyst design and/or catalyst selection.

The chemical reactions that are of primary interest in the catalytic processing of heavy oils are: (1) desulfurization, and (2) demetallization. In some cases, the removal of nitrogen compound is another important reaction, particularly when the gas oil fraction is used as feedstock for a fluid catalytic cracker or for hydrocracking. During the cycle, the catalyst system deactivates due to coke deposition and metal poisoning that is often represented as occurring in three phases:

1. Coke deposition on the fresh catalyst system;
2. Constant deactivation rate that is influenced by metal deposition from the feedstock during which nickel and vanadium fill up the pores and block active sites;
3. Rapid deactivation again and is caused by the final constriction of the catalyst pore mouths by metal deposition.

Thus, typically, catalysts for heavy oil processing require large pore volumes for high efficiency and tolerance to the feedstock constituents. High catalyst pore diameters are needed to minimize the diffusion constraints. Highly porous, low surface area catalysts have favorable transport properties and have high metals capacities and resistance to pore plugging. However, the hydrotreating activity of such catalysts is relatively low. Less porous, high surface area catalysts have a higher hydrotreating activity, but are more susceptible to deactivation through pore-mouth plugging. Thus, an optimum balance in metals capacity and hydrotreating activity is necessary to optimize the catalyst load and maximize catalyst life cycle.

Hydroprocessing catalysts typically have smaller pore diameters, a lower pore-size distribution, high surface area and high hydrotreating activity. As these catalysts are more susceptible to pore mouth plugging, they have to be protected by upstream hydrodemetallization catalysts.

When the ratio of the intrinsic hydrodemetallization activity to the asphaltene diffusion into and through the catalyst pore structure is high, the metals will be removed from their organic environment towards the pore mouth, restricting diffusion of reactant species into that pore and plugging the pore. Thus, there is an optimum balance of hydrodemetallization activity and diffusion properties for guard bed hydrodemetallization catalysts. Excessive pore mouth blockage can occur when the hydrodemetallization catalyst is operated at a too high temperature at the initial (high activity) phase of an operational cycle. Excessive pore mouth blockage can also occur when high hydrodemetallization acidity catalysts process feeds with highly reactive metal contaminants.

To meet the objectives of heavy oil hydrotreating, it is critical that the appropriate volumes of demetallization and high activity catalysts are loaded into the reactor(s). Since the reactors have a fixed volume to load catalyst, a short load of hydrodemetallization catalyst will result in a premature deactivation of the high activity tail end catalyst section due to poisoning by nickel plus vanadium deposition. An excess of hydrodemetallization catalyst does not enhance the process and often results in low hydrotreating activity and loss of process efficiency, even to the extent of premature shut down of the operation.

Finally, the absolute response in temperature with respect to time is different for different heavy oil hydrotreaters. The units are operated until the catalysts are completely deactivated by coke and metals. The last stage of deactivation is intentionally avoided in commercial operations thereby reducing the potential for a sudden shut down. As the reactions are exothermic and higher temperature causes an increase in deactivation rates, hydrogen quench between reactors and/or catalyst beds is applied to adjust the inlet temperatures.

5. Process options

Establishing the state of the asphaltene particles in the original heavy oil and the changes that occur during processing is the basic requirement in the scientific quest to find a solution to the irreversible deposition of coke precursors. Indeed, modeling efforts that describe the phase behavior of asphaltenes in heavy oil and in reacted heavy oil should take into account the physical and molecular characteristics of asphaltene constituents in the original (unreacted) heavy oil and in the reacted heavy oil. This information will assist in the development of suitable processes and process catalysts.

First, coker operations are profitable but produce unstable liquids and low-value coke. Second, attempts to increase conversion of heavy oil during visbreaking will bring on the formation of polar and/or high molecular weight species leading to sediment formation and deposition. The chemistry involves the occurrence of reactions that are irreversible. Once these reactions have occurred, phase separation is inevitable and deposits are formed. The use of a solvent as part of the reaction mix may delay phase separation for a short time but they (solvents) are of limited use. Once the chemical reactions have produced the insoluble polar organic degradation products, phase separation is inevitable, whatever the nature of the added solvent. Therefore, the key to delaying the onset of phase separation is control of the chemistry through the use of hydrogen and carbon-tolerant catalysts. However, it is not that straightforward and process design outside of the typical hydroprocessing operational parameters is necessary.

Hydroprocesses are also favorable for primary upgrading [3,6]. However, the constituents of heavy oil (that lead to formation of sediment in thermal processes) are deleterious to catalyst activity and to on-stream lifetime. Therefore, there is the need to develop catalysts that are tolerant to the constituents of the feedstocks. Indeed, efficient conversion of heavy oils requires not only serous efforts to develop adequate catalysts but also improved understanding of catalyst structure and preparation.

Since coke formation is related to the chemical reactions of the asphaltenes (and other) constituents during thermal cracking, the answer to mitigate coke formation is to understand reaction kinetics as well as process design and reactor design. Reactor hydrodynamics such as heating rate, final temperature, residence time and gas phase composition are the variables controlling the coking process. This may also require a change in thinking of process parameters as well as the modification of existing, or the development of new, processes to respond to market demands.

The issue of phase separation of coke precursors during heavy oil conversion must be addressed. Chemically, preventing the rapid and irreversible reactions that lead to incompatibility and insolubility of the reacted constituents can eliminate phase separation. Hydroconversion of the asphaltene constituents by increasing the partial pressure of hydrogen is one option. Development of catalysts that are more tolerant to coke deposition and metals deposition is another option. Recycling a specific fraction that has a higher solvent power for the asphaltenes constituents and their reacted products is another option.

Deasphalting or deasphaltening the heavy oil solves the problems related to premature solids depositions. Reaction rates are increased and the majority of the fouling problems are eliminated. However, the issue of disposal of the asphalt or asphaltene fraction remains.

In addition to the visbreaking and coking processes, there are a variety of process options [6] that have been developed within the last two decades and many of which are now seeing on-stream activity. Further development of these and other concepts is needed to enhance the conversion of heavy oil. Alternative processes are also available. These involve coupling a hydroconversion process with a coking or visbreaking unit. The converted residue from the hydrocracker is sent to the coker, where a portion is converted to distillate. This procedure combines the benefits of higher liquid yields from hydrogen addition with the low cost of a coker.

As noted above, the increased conversion of heavy oil during visbreaking will bring on sediment deposition. However, this can be changed by the use of hydrovisbreaking. In fact, hydrovisbreaking is receiving some attention as a possible alternate to visbreaking and coking. By feeding unconverted heavy feedstock to the hydrovisbreaker or hydroconverted heavy feedstock to the coker, the overall yield of high-value products is maximized and the yield of low-value coke is minimized. Further development of these and process other concepts are needed to enhance the conversion of heavy oils.

Until catalysts are developed that will handle heavy oil feedstocks, the immediate need is to consider an evaluation of the process parameters. The need to separate metallic constituents and coke precursors from the feedstock is also a major issue because of the need to dispose of such rejects. Alternatively, a step-down in process severity might be on order. This, obviously, could increase reaction times but might allow controllable chemistry and moiré efficient use of the hydrogen content of the feedstock.

The options include the choice between (1) a single stage upgrader (conversion) followed by the usual product hydrotreating and (2) a multi-stage process.

The two-stage process might allow temperature control and a higher degree of hydrogen management. In fact, introduction of hydrogen into the reactor at the earliest possible opportunity can have a very beneficial effect. For example, hydrotreating Athabasca bitumen at 380 °C (715 °F) yields 5% (w/w) coke (as opposed to delayed coking that yields 17–20%, w/w, coke) [41]. The asphaltene content of the bitumen is reduced from 17% (w/w) in the original feedstock to 4% (w/w) in the liquid product. Further treatment by choice of a suitable second process of choice could result in a balance between process economics and products.

Other work has shown that hydrotreating a 15° API heavy oil followed by fluid catalytic cracking of the product reduces the coke yield from 10% (w/w) to 7% (w/w). Similarly, hydrotreating a 7° API residuum followed by delayed coking of the product reduces the coke yield from 30% (w/w) to 18% (w/w).

While such process options or modifications may not be the ultimate answer, they are certainly a move in the right direction. However, the balance between additional hydrogen costs and process costs to product slate has to be considered and given attention.

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