Petroleum Residue Upgradation via Visbreaking: A Review

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Worldwide petroleum residue processing capacity has reached about 810 MMTPA. In the present petroleum refining scenario, the viability of a petroleum refinery strongly depends on the flexibility of processing heavy crudes and, in turn, heavy residues. Visbreaking is one of the major residue upgrading processes and constitutes about 33% of the total residue processing capacity. In the present communication, the published literature pertaining to the visbreaking process has been extensively analyzed and a state-of-the-art review has been written that includes the following: (i) the effect of feed properties on fuel oil stability; (ii) reaction pathways, mechanism, and kinetics; (iii) parametric sensitivity of the operating variables such as temperature, pressure, and residence time; (iv) different visbreaker designs, viz. coil visbreaker, coil-soaker visbreaker, soaker with internals, and high conversion soaker; (v) coking and fouling; (vi) estimation of design parameters, viz. gas holdup in high-pressure bubble column (soaker), gas holdup in sectionalized bubble column (soaker with internals), liquid-phase mixing and axial mixing in high-pressure bubble column, liquid-phase mixing and axial mixing in sectionalized bubble column, and weeping; and (vii) mathematical modeling of visbreaker, which mainly includes the coil and the soaker. An attempt has been made to get the aforementioned aspects together in a coherent manner so that the information is available at a glance and is expected to be useful to researchers and practicing refiners.

1. Introduction

The worldwide petroleum refining capacity has reached about 4100 million metric tons per annum (MMTPA),† inclusive of India’s refining capacity of about 146 MMTPA,‡ processed in over 700 refineries.‡ Petroleum refining has entered a significant transition period as the industry has moved into the 21st century. The decreasing supply of light sweet crude oils is a matter of serious concern for the petroleum industry because the distillation of heavy crude oils leaves behind a significant amount of vacuum residue (about 40% of the total crude processed).§ The quantity of heavy residues is expected to increase in the future in view of the progressively increasing heavier nature of the crudes.‖ In order to satisfy the changing pattern of product demand, significant investment in the refining conversion processes has become inevitable to profitably utilize these heavy crude oils. Although the most efficient and economical solution to this problem depends, to a large extent, on individual country and company situations, the most promising technologies involve the conversion of vacuum residua and extra heavy crude oil into light and middle distillate products. It has been widely envisaged that the window of opportunity is for those refineries that can process low-grade crudes to produce high-grade products. Another reason for giving extra attention to petroleum residue upgradation is that, with the continual increase in the crude oil prices, it has become imperative to get the maximum out of the residual feedstocks. In the light of this scenario in the petroleum refining industry, petroleum residue or bottom-of-the-barrel upgradation has gained tremendous importance. The processes that convert these residues into low-boiling, value-added products are called as bottom-of-the-barrel upgradation processes or residue upgradation processes.
Table 1. Typical Yields from Bachaquero or Light Arabian Crude Oil (Basis = 2.65 MMTPA Crude Oil)\textsuperscript{18}

<table>
<thead>
<tr>
<th>Process</th>
<th>Crude Unit Operation</th>
<th>Visbreaker Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U.S.</td>
<td>Japan</td>
</tr>
<tr>
<td>Crude Unit Operation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>residual flow rate, MMTPA</td>
<td>1.94</td>
<td>1.28</td>
</tr>
<tr>
<td>cutter needed (no visbreaker), MMTPA</td>
<td>0.52</td>
<td>0.92</td>
</tr>
<tr>
<td>total no. 6 fuel oil production, MMTPA</td>
<td>2.46</td>
<td>2.20</td>
</tr>
<tr>
<td>Visbreaker Operation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>visbreaker yields, wt %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}–C\textsubscript{4}</td>
<td>2.4</td>
<td>2.0</td>
</tr>
<tr>
<td>C\textsubscript{5}–C\textsubscript{17}</td>
<td>6.2</td>
<td>5.5</td>
</tr>
<tr>
<td>175–343 °C</td>
<td>20.6</td>
<td>10.5</td>
</tr>
<tr>
<td>343 °C+</td>
<td>70.8</td>
<td>82</td>
</tr>
<tr>
<td>residual flow rate, MMTPA</td>
<td>1.37</td>
<td>1.05</td>
</tr>
<tr>
<td>cutter needed, MMTPA</td>
<td>0.17</td>
<td>0.66</td>
</tr>
<tr>
<td>total no. 6 fuel oil production, MMTPA</td>
<td>1.54</td>
<td>1.71</td>
</tr>
</tbody>
</table>

2. Qualitative Description of Different Upgrading Processes

Technologies for upgrading heavy feedstocks such as heavy oil, bitumen, and residua can be broadly divided into carbon rejection and hydrogen addition processes. Carbon rejection redistributes hydrogen among the various components, resulting in fractions with increased H/C atomic ratios and fractions with lower H/C atomic ratios. On the other hand, hydrogen addition processes involve reaction of heavy feedstock with an external source of hydrogen that results in an overall increase in H/C ratio. Within these broad ranges, all upgrading technologies can be subdivided as follows:

(1) Carbon rejection processes: visbreaking, steam cracking, fluid catalytic cracking, and coking.

(2) Separation processes: solvent deasphalting.

(3) Hydrogen addition processes: hydrocracking, fixed-bed catalytic hydroconversion, ebullated catalytic bed conversion, hydrovisbreaking, hydropyrolysis, and donor solvent processes.\textsuperscript{20}

Table 2 shows the world residue processing capacity in different parts of the world. It can be seen that a major portion of the petroleum residue upgrading (about 63%) is met via thermal processes, viz. visbreaking and delayed coking.

<table>
<thead>
<tr>
<th>Crude Unit Operation</th>
<th>Visbreaker Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feasibility region of the commercial residue conversion processes (Phillips and Liu\textsuperscript{22}).</td>
<td></td>
</tr>
</tbody>
</table>

that, in the long run, solvent deasphalting, as a stand-alone residue upgrading process, will have less interest worldwide.\textsuperscript{21}

Residue fluidized catalytic cracking (RFCC) involves a vapor-phase catalytic cracking reaction. The heavier and more contaminated atmospheric and vacuum residues cannot vaporize and eventually end up getting deposited on the surface of the catalyst and tend to increase the production of coke and deactivate the catalyst. Thus, residue fluidized catalytic cracking (RFCC) is limited in terms of its applicability to process relatively low metal and low asphaltene feeds.\textsuperscript{17}

Residue hydropyrolysis can process slightly heavier and high metal content feedstocks (Conradson carbon residue (CCR) up to 10 wt % and metals up to 100–150 ppm) with the aid of a new process such as Chevron’s Onstream Catalyst Replacement (OCR) and Shell’s HYCON unit. Thus, residue hydropyrolysis has a distinct advantage over residue fluidized catalytic cracking as regards the processing of heavier feeds. However, it may be pointed out that, although residue hydropyrolysis can produce high-quality products and meet the requirement of the reformulated gasoline and diesel in terms of low aromatic and low sulfur, hydrogen resource and high investment limit its application.\textsuperscript{17} Thus, heavy residues containing more than 10 wt % CCR and 150 ppm of metals can only be processed by using noncatalytic carbon rejection processes\textsuperscript{22} as illustrated in Figure 1.

3. Visbreaker Feed Properties

Petroleum residua comprise a polarity continuum of molecules ranging from nonpolar hydrocarbons to intermediate polarity aromatic species to polar asphaltenes, and possibly very polar pre coke materials. In the visbreaking process, the nature and behavior of the asphaltenes determine potential fuel oil compatibility.\textsuperscript{7} Cracking temperatures used in visbreakers must be
carefully controlled to prevent separation of the asphaltenes from the bulk of the visbroken residue (fuel oil). Asphaltenes are normally held in colloidal suspension by complex peptizing agents, which occur naturally in crude oil. Under severe cracking conditions, these peptizing agents tend to be broken down, which in turn leads to asphaltenes precipitation. As a result of this phenomenon, the visbroken residue becomes unsuitable for sale as fuel oil. This problem is usually referred to as fuel oil instability.23,24

For a given feed, the visbreaking conversion is proportional to the cracking temperatures and residence times; however, it is limited by the induction of the instability in the residue followed by asphaltenes flocculation, which ultimately leads to the coke formation.25 An unstable feed, defined by the existence of \( n \)-alkane insoluble material separated from the maltene (oily) phase, along with the formed coke leads to fouling of the process lines and the furnace heater tubes. This results in the incomplete combustion of the fuel oil and an early shutdown of the units (shorter run length).

At molecular level, the stability factor, the coking tendency, and, consequently, the permissible conversion (crackability) are the typical characteristic features of the feed being processed to visbreaker units.26 The feed properties vary to a large extent depending upon (i) the crude origin and (ii) the extent of topping. To understand the fundamental chemistry of the cracking behavior, the induction of instability, the coke formation, the reaction mechanism and kinetics, and the product variation as a function of the feed properties, a large number of AR, VR, their asphalts, and bitumen have been processed either in continuous or batch manner.27–39 These feedstocks have a range of H/C ratios from 1 to 1.8, API gravity from 3 to 18, sulfur content from 0.1 to 7.5 wt %, and asphaltene content in the range of 0.6–16 wt %. Parts A–F of Figure 2 show the variation in the feed properties as a function of API gravity and H/C atomic ratio of the feed. From these figures, the following can be seen:

1. The sulfur and nitrogen content decreases with an increase in the H/C atomic ratio (parts A and B of Figure 2), which indicates the increasing concentration of these heteromoieties in aromatic and unsaturated compounds.

2. The H/C atomic ratio decreases with a decrease in the API gravity (Figure 2C). The reduction in this ratio indicates an increase in the content of unsaturated and polycondensed aromatic compounds. This is again confirmed by the observed trends of Conradson carbon residue (CCR) and \( n \)-C\(_7\) insoluble asphaltenes (parts D and E of Figure 2).

3. H/C atomic ratio decreases linearly with an increase in CCR (Figure 2F). The linear relation24 between CCR and H/C ratio is given by

\[
H/C = 1.71 - 0.0115\text{CCR} \tag{1}
\]

Equation 1 holds within two limits; at H/C = 1.71, the CCR = 0, i.e., no coke formation, while at H/C ratios = 0.5, the CCR = 100 (which means all material gets converted to coke under test conditions). The correlation is based on 114 data

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**Figure 2.** Variation in feed chemical composition and physical properties.
points derived from 15 different crudes and has a correlation coefficient of 0.988.

In order to ease the identification of chemical composition, heavy oil can be classified as consisting of four polarity and solubility classes of components, viz. saturates, aromatics, resins, and asphaltenes (SARA). Prior to chromatographic separation, asphaltenes can be separated. Asphaltenes are typically defined as the component that is insoluble in n-heptane and soluble in toluene. Using normal-phase chromatography, the heptane-soluble maltene material can be separated into saturates, aromatics, and resins using heptane, toluene, and toluene/methanol mixtures, respectively. The qualitative relation between the feed characteristics and their permissible conversion, product yield, stability, and coking tendency can be summarized as follows:

1. The viscosity reduction (with high distillates production) largely increases with an increase in the extent of conversion for a given feed with specific characteristic properties.

2. The extent of permissible conversion of a particular feed within which it is stable and has no coke yield is termed as “crackability.”

3. The stability and the crackability of the feed are found to improve with an increase in the content of the resin-to-asphaltene ratio and with a decrease in relative aromaticity between the maltene phase (oily phase) and the asphaltenic phase.

4. Feeds rich in asphaltene contents and CCR are found to produce higher gas, gasoline, and coke yields.

The quantitative description between the feed characteristics and conversion, yield, stability, and coke has also been proposed. Kuo reported that the extent of conversion (crackability) is proportional to the feed aromatics and the resin content and inversely proportional to the saturates and the CCR content. The author proposed the following quantitative relationship:

\[
K_c = (H/C)^{-3.80}(M_w)^{0.40}
\]

Katarya et al. reported the batch thermal cracking of six different vacuum residues and asphalts. The authors found the distillate (VGO, LGO, Ga, G) yield to be dependent on the severity and the initial feed concentration (SARA, n-C5 insolubles, n-C7 insolubles, CCR, and S) composition as follows:

\[
VR = 100\left(\frac{As}{Sa}\right)^{0.026}\exp\left[-0.023\left(1 + \frac{n-C_C}{CCR}\right)SI\right]
\]

\[
VGO = 4.76(SI)^{0.5}\left(\frac{n-C_5}{S + CCR}\right)^{0.96}
\]

\[
LGO = 3.24(SI)^{0.77}\left(\frac{Sa}{NA}\right)^{0.13}
\]

\[
Ga = 0.271(SI)^{0.19}\left(\frac{As}{PA}\right)
\]

\[
G = 0.43(SI)^{0.45}\left(\frac{n-C_C}{CCR}\right)
\]

These correlations are based on batch studies at relatively low severity (temperature = 400–430 °C and residence time = 3–60 min).

Apart from the feed characteristics, the mode of operation also acts as another important factor that governs the product yield and the stability. Thus, continuous improvements are being made in the thermal unit operation to achieve economical and improved conversions with desirable product selectivity.

4. Kinetics and Mechanism of Visbreaking Reactions

4.1. Structural and Compositional Changes during Visbreaking. Low demand for the fuel oil has forced the refiners to opt for higher conversion even for feeds with low crackability. In order to achieve this, the fundamental understanding of the reactions involved rendering instability, and the subsequent coke formation is needed. The pertinent subject has been elaborated in the following three sections: (i) the feed characteristics, (ii) the induction of instability and its mechanistic variation, and (iii) the coke formation and fouling.

4.1.1. Feed Characteristics: Salient Features. Visbreaker feeds comprise saturates, aromatics, resins, and asphaltenes and are classified on the basis of their solubility and chromatographic separations. In order to characterize these fractions, their average molecular weight (\(M_w\)), average molecular formula, microcarbon residue (MCR) content, and the two important structural features (using H1 and C13 NMR techniques), viz. aromatic and aliphatic carbon content, are taken into consideration. These features fairly distinguish subcomponents from each other and their variation within a class from different sources of visbreaker feeds. As thermal treatment progresses, the solubility parameter of the components of residua fractions increases, and the apparent molecular weight decreases. The distinguished features of these subfractions can be summarized as follows:

\[(1)\] Saturates: These components are found to have an average carbon number in the range \(C_{38-50}\) with relatively low heteroatom content. The structural study shows that it consists of long alkyl chains with few or negligible naphthenic and aromatic rings. The microcarbon residue (MCR) value (coking tendency) reported is almost 0 wt %, which indicates that these fractions are completely volatile and cannot directly yield coke.
(2) Aromatics: The aromatics are found to have a carbon number in the range C_{41}–C_{53}. These are simple structures compared to resins and asphaltenes, having low heteroatom content and MCR value of about 3.7 wt %.

(3) Resins: These are viscous, tacky, and volatile enough to be distilled with hydrocarbons. Structurally, resins consist of an appreciable amount of aromatic carbon content (40–53%) with intermediate paraffin chain length on naphthenic structures and aromatic rings, and about 2/3 of its aromatic carbon atoms are nonbridged. The resin fraction acts as the dispersant for the asphaltic component in the maldene phase.

(4) Asphaltenes: Asphaltenes are the heaviest and most polar class of component in the crude oil, containing larger amounts of heteroatoms than the rest of the components in the crude oil.\(^{41,52}\) Asphaltenes comprise molecules with 4–10 pericondensed aromatic rings, 4–6 alkyl carbon chains, and 20–24 aliphatic carbons, with an average H/C atomic ratio of about 1.2. IR studies have shown that about 90% of the hydrogen is substituted on saturated carbon, primarily in methylene and some methyl groups. Sulfur species are primarily aromatic thiophenes and aliphatic sulfides. Nitrogen species are primarily aromatic pyrrole and pyridinic and metal chelating (Ni, V) porphyrin or pseudoporphyrin type of structures.\(^{53}\) The average molecular weight of an asphaltene component molecule is 750 g/mol, with a range of 500–1000 g/mol.\(^{41}\) Groenzin and Mullins\(^{42}\) employed the time-resolved fluorescence depolarization (TRFD) technique to estimate the molecular weight of asphaltenes. TRFD can be performed on extremely dilute solutions (10 mg/L)\(^{41}\) and, hence, does not suffer from aggregation and gives the true molecular weight of asphaltenes. It may also be pointed out that the mass spectral ionization techniques, viz. field ionization mass spectrometry (FIMS), electrospray ionization (ESI), atmospheric pressure photo ionization (APPI), and atmospheric pressure chemical ionization (APCI) employed for the determination of molecular weight of asphaltenes corroborate the TRFD results.\(^{54}\)

The extent of asphaltenes aggregation depends on the type of solvent, the temperature, and the concentration. It has been found that molecular association may occur even at a very low concentration (150 mg/L).\(^{54}\) Vapor pressure osmometry (VPO) and gel permeation chromatography (GPC) suffer from the fact that a high concentration of asphaltenes in solution (about 1000 mg/L) is needed, which leads to the formation of aggregates or micelles of asphaltenes and not individual molecules, which in turn gives rather large estimations of asphaltenes molecular weight (nearly 10000 g/mol).\(^{54}\) It is known that asphaltenes are in a very delicate state of dynamic equilibrium, where a minute asphaltene droplet is covered by a sequential envelopes of resins,\(^{55}\) aromatics, and saturates (Figure 3) with decreasing\(^{55}\) polarity. According to this model, asphaltenes are dispersed by the surfactant-like property of resins that in turn are held in the solution by aromatics. Saturates are nonsolvents for the asphaltenes. It may also be pointed out that, though the asphaltenes are not soluble in petroleum without the resins,\(^{40}\) the resins might be a cosolvent. However, amphiphilic model compounds increase the solubility of asphaltenes, and the addition of resins reduces the asphaltene radius of gyration measured by small-angle X-ray scattering.\(^{55}\)

### 4.1.2. Mechanistic Variation and Instability

**Cracking**

Dehydrogenation, H-abstraction, cyclization, aromatization, and condensation are the major reactions that occur within the molecules during thermal processing of the feed.\(^{14}\) The feeds rich in paraffin content are found to give high gas oil yield via \((\text{C}_{41}–\text{C}_{53})\), BDE = 98 kcal mol\(^{-1}\)) splitting reactions,\(^{31,38}\) while feeds rich in resin and asphaltenes contents are found to undergo dealkylation \((\text{C}_{m}–\text{C}_{al}, \text{BDE} = 78 \text{ kcal mol}^{-1})\) to give high yields of gas, gasoline, low carbon molecules, and coke (at high severity via condensation). Typical structural variation in the subcomponents of the residue during thermal cracking\(^{46,56}\) can be summarized as follows:

1. There is a reduction in the paraffin chain length from \(\text{C}_{50}\) to \(\text{C}_{50}\) in saturates.

2. There is dealkylation of the aromatics and resins (polar components), resulting in a decrease in the number of carbon atoms per alkyl chain (reduction in chain length) with parallel reduction in the naphthenic rings. The simultaneous increase in the carbon number indicates their intermolecular condensation reactions.

3. Quantitatively, there is an increase in saturates content (due to thermally formed distillates), a reduction in the aromatic and resin content, an increase in highly polar asphaltene content, and a change in the internal polarity distribution within the asphaltenes themselves. At a particular conversion, the thermodynamic colloidal stability of the oil gets disturbed, which in turn leads to the separation of the asphaltenes from the maldene phase and the feed becoming unstable. The plausible mechanism of the asphaltene aggregation involve (a) \(\pi–\pi\) overlap between aromatic sheets, (b) hydrogen bonding between functional groups, and (c) other charge-transfer interactions.\(^{55}\)

**Fuel oil stability** is the most important factor that governs the possible yield of the liquid products from the visbreaking process. The feed residue and the visbroken residue (500 °C+) obtained by distillation are analyzed for their stability by the standard merit number test (IFP-3024-82, severity test for thermal reactions by spot method and residue stability determination). For this purpose, 2 mL of sample is diluted with 10 mL of a mixture of o-xylene and 2,2,4-trimethylpentane with variable o-xylene content. The above mixture of the sample and the diluent is homogenized with the help of a glass rod. The homogeneous mixture is spotted on Whatman filter paper no. 2. The spot is visually evaluated for its homogeneity or phase separation. For homogeneous samples, the stability is indicated by the lowest volume of o-xylene added in a mixture of o-xylene and 2,2,4-trimethylpentane. The spot with a markedly darker center (appearance of two phases) is considered as an unstable sample. Samples with merit number less than 7 are considered to be stable samples, those with merit number 7–8 are taken as borderline, and those with merit number above 7 are considered to be unstable samples. For necessary fuel oil specifications, the merit number test is carried out for 150 or 350 °C+ bottoms fractions.
A solubility parameter is a kind of cohesion parameter that describes the interaction between molecules in condensed materials. It could be expressed as the difference between the internal energy of the condensed material and that of an ideal gas of the same material at the same temperature. It may be pointed out that the main purpose of the solubility parameter concept has been to predict the precipitation of asphaltenes. The complexing solubility parameter component measures the interaction energy that requires a specific orientation between an atom of one molecule and a second atom of a different molecule. The field force solubility parameter component measures the interaction energy of the liquid that is not destroyed by changes in the orientation of the molecules. Thus, hydrogen bonding and electron donor—electron acceptor interactions are part of the complexing solubility parameter component, and van der Waals and dipole interactions, when significant, are part of the field force solubility parameter component. It may be pointed out that the solubility of an individual asphaltene moiety decreases with the increase in the difference between solubility parameters. Also, a lower molecular weight moiety is more soluble than the higher molecular weight molecule for a particular difference in solubility parameter. The solubility depends on both molecular weight and polarity of the particular asphaltene molecule or associated specie. As thermal treatment proceeds, the solubility parameter of the components of the residue increases and the molecular weight decreases. An unstable system results when the depletion of the resins diminishes the ability of the asphaltenes/resins complexes to increase their apparent molecular weights to autoadjust their solubility parameter to closely match the solubility parameter of the matrix. It is at this stage that a bimodal system is formed and the onset of coking takes place.

Apart from the thermal induction of instability, the external parameters are also found to affect the asphaltene precipitation. Nielsen et al. observed that, with an increase in the temperature, the molar mass of the oil and the diluent/oil ratio results in a larger amount of asphaltene precipitation. On the contrary, an increase in the pressure or the number of carbon atoms in the diluent molecules results in a lower amount of asphaltene precipitation. Further, the distinct features of the stable and unstable feed and coke formation include the following:

1. Structural and the characteristics variations: The asphaltenes and resins in an unstable feed are found to have low H/C ratio, high aromaticity, highly condensed aromatic rings, and less alkyl and naphthenic substitution. Figure 4 shows three idealized molecular structures for asphaltenes, which depict the possible interaction of the aromatic moieties with aliphatic chains and heteroatoms. The instability of asphaltenes increases with increasing heteroatom content (O, N, and S) and metal content (Ni and V) in the parent feedstock.

2. Charge on asphaltenes and resins: Fotland et al. observed that a stable feed (asphaltene content of 0.3–9 wt %) under the influence of dc electric voltage shows little (0.015–0.05 μS/m) or no conductivity, while an unstable feed showed large conductivity (0.1–0.32 μS/m). The conductivity (also confirmed by the gravimetry test) was also found to be proportional to the extent of instability induced by the precipitation of the asphaltenes using varying amount of externally added paraffinic solvent. Later, it was also confirmed by the electrodeposition study (at constant voltage 3.6 kV) for the crude oil, fuel oil, AR, VR, and visbroken residues at different temperatures. Further, the author extended the study to separated resins and asphaltenes from the residue and found that the micelle structure consists of negatively charged resins surrounding a positively charged asphaltene core. The study also concluded that stability of the feed is highly dependent on (i) peptizability (aromaticity) of asphaltene core, (ii) peptizing power of the resins, (iii) relative amount of the asphaltenes and the resins, and (iv) aromaticity of the maltene phase.

The physical changes and heteroatom (S, N, Ni, V) distribution that occur as the consequence of the thermal cracking include the following:

1. Physical changes: The feeds with high initial viscosity (and high sulfur content) undergo high viscosity reduction, due to cross-linking within different components by weak bonds that can easily break, as compared to the feeds with lower starting viscosity. Similarly, feeds with low sulfur content (<1%) resulted in a sharp increase in the asphaltene content as...
compared to the feeds with high sulfur content (\(>1\%\)). The pour point and density reduction were found to be proportional to viscosity reduction.

(2) Thermal effects on heteroatom: Nitrogen in the feed exists in two forms, i.e., basic (30\%) and nonbasic, and is mostly concentrated in the resins and asphaltenes of the residue before and after the thermal conversion.\(^6\) The denitration is less susceptible to cracking and remains concentrated in the liquid fuel, showing continuous rise in N/C ratio with increasing C-rejection conversion. The sulfur content and H/C ratio in the visbreaker has been observed to reduce with an increase in the conversion.\(^{14,28,30,31,56}\) The loss in sulfur can be attributed since heavy residues are notorious coke producers in cracking processes. The effects are even more pronounced if the residue is heavy due to coke precursors. Thus, heavy boiling material mainly undergo dealkylation and condensation reactions that give rise to coke precursors.\(^{4,12,28,30,31,56}\) The sulfur compounds, i.e., dimethyl sulfide (DMS), dimethyl disulfide (DMDS), benzothiophene, etc., act as metal passivators and also alter the rate of radical reactions through their interference with H-atom transfer and termination reactions. Similarly, phosphorus-containing compounds, such as triethyl phosphate (TEP), triphenyl phosphate (TPP), benzyl diethyl phosphate (BDP), and triphenyl phosphate sulfide (TPPS), can be used as metal passivators and for facilitating easy removal of coke during decoking operations (decoking time can be drastically reduced). The use of alkali metal compounds such as \(\text{K}_2\text{CO}_3\), \(\text{Na}_2\text{CO}_3\), \(\text{K}_2\text{O}\), \(\text{Na}_2\text{O}\), and \(\text{Na}_2\text{SO}_4\) also promotes the gasification of coke during decoking operations.

4.1.3. Coke Formation and Fouling. Thermal cracking of hydrocarbons is always accompanied by the fouling and coke formation that deposit on the furnace walls and results in increased pressure drop, reduced heat transfer rates, hot spot formation due to uneven flow distribution, and corrosion by carbonization. The detrimental effects arising out of these phenomena are reduced run length, reduced selectivity, production losses, and high maintenance, operating, and utility costs. The effects are even more pronounced if the residue is heavy since heavy residues are notorious coke producers in cracking coils.\(^8\) The fouling process progresses through various steps, viz., polymerization of unsaturated radicals, dehydrogenation, subsequent increase in pressure, contraction, and their final conversion into coke. The prevailing mechanisms in this process include (1) catalytic growth and (2) radical mechanism for carbon deposition.\(^{63}\)

(1) Catalytic growth: The tube metallurgy plays an important role in this kind of mechanism. During the start-up, the exposed active metal sites (Cr, Ni, Fe, etc.) in the furnace coils act as a heterogeneous polyaddition catalyst, resulting in initial fouling deposition by polymerization of the molecules containing olefins. Once the uniform film is formed on the metallic surfaces, the catalytic growth mechanism is controlled by the diffusion of the monomers into the polymeric layer, which is dependent on the degree of cross-linking. Thus, after the initial cracking period of 15–20 days, the phenomenon of catalytic growth becomes insignificant in the visbreaking coils due to metal surface adsorption.

(2) Radical and condensation mechanism: The polyaromatic (polymeric) films formed on the metal surface still contain few saturated centers. The hydrogen abstraction of these species by free radicals thus becomes a significant reaction. The further growth in the film occurs through the addition of an olefin or new free radical in the feed. The katable condensed aromatic layers result in the hard coke formation, which is usually difficult to remove during decoking of the furnace coil and transfer line exchangers. Adding to this, the asphaltens from the entrapped heavy boiling material mainly undergo dealkylation and condensation reactions that give rise to coke precursors. Thus, further dehydrogenation (H/C tends to reduce \(<0.5–0.6\)) with a subsequent increase in pressure and increase in the thermal conductivity of the coke produced with unavoidable porosity.

Refineries frequently use different techniques, such as additive inhibitors, surface treatment, and changes in the tube metallurgy and physicochemical characteristics of feedstock, to combat the fouling problem in furnace coils and transfer line exchangers. Though most of these techniques are practiced for high-temperature pyrolysis processes (such as steam reforming, naphtha pyrolysis, and ethane cracking), they can also be extended for mild thermal cracking process such as visbreaking.\(^6\) The methodology can be briefly described as follows:

4.1.3.1. Additive Inhibitors. The sulfur compounds, i.e., dimethyl sulfide (DMS), dimethyl disulfide (DMDS), benzothiophene, etc., act as metal passivators and also alter the rate of radical reactions through their interference with H-transfer and termination reactions. Similarly, phosphorus-containing compounds, such as triethyl phosphate (TEP), triphenyl phosphate (TPP), benzyl diethyl phosphate (BDP), and triphenyl phosphate sulfide (TPPS), can be used as metal passivators and for facilitating easy removal of coke during decoking operation (decoking time can be drastically reduced). The use of alkali metal compounds such as \(\text{K}_2\text{CO}_3\), \(\text{Na}_2\text{CO}_3\), \(\text{K}_2\text{O}\), \(\text{Na}_2\text{O}\), and \(\text{Na}_2\text{SO}_4\) also promotes the gasification of coke during decoking operations.

4.1.3.2. Surface Treatment. This method reduces the catalyzing tendency of the reactor surfaces by treatment with hydrogen, dilute acids (HCL, \(\text{H}_2\text{SO}_4\)), and sulfides. Also, a preoxidation step is practiced during the start-up of new coils, which results in stable and adherent \(\text{Cr}_2\text{O}_3\) film on the coil surface.

4.1.3.3. Tube Metallurgy. The key considerations in selecting appropriate tube metallurgy are oxidation, carburization, creep strength, high-temperature ductility, and cost. The higher weight percentage of Ni and Fe in tube metallurgy accelerates the dehydrogenation reactions at elevated temperatures, thereby increasing the coking rates of hydrocarbons. To overcome this, the formation of an oxide film on the tube-wall surface is desirable to minimize the metal effects. The elements Cr, Ni, and Si act as effective barriers for carburization. Similarly, the stability of oxides formed varies in the following order: \(\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{SiO}_2 > \text{Cr}_2\text{O}_3 > \text{SiO} > \text{Mn}_2\text{O}_3 > \text{Mn}_3\text{O}_4 > \text{FeO} > \text{Fe}_2\text{O}_3 > \text{NiO} > \text{Cr}_2\text{O}_3\).

4.1.3.4. Polishing. The polishing of tube surfaces results in reduction in irregularities, the active metal sites (due to removal of surface irregularities), and emittance of the surface. The emittance, which influences radiation and, therefore, the temperature of reactor surface, may vary from below 0.1 for a polished surface up to 0.9 for a plain or carbonized surface. For highly polished tubes, the lower emittance means lowering of tube-wall temperature by \(50–100\) \(\text{°C}\) and, hence, lowering of the coking rates.

4.1.3.5. Alonizing. Coating the surface with aluminum can be an attractive remedy for preventing carburization of furnace coils. The alonized surfaces show (i) little or no loss of tube material, (ii) no change in the roughness, (iii) a higher percentage of Cr, Al, Nb, and Si, and (iv) higher thermal conductivity of formed coke.

4.1.3.6. Effect of Feed Composition. The physicochemical properties of the feedstock are also found to affect the coking rates and their properties. Yan\(^47\) studied the coke-forming tendency of three different feeds and found that coking tendency follows the following order: mixed residue \(<\text{Boscan crude}\ <\text{Arabian heavy residue}\). The study concluded that visbreaker should be operated at maximum feasible operating temperature with shorter residence time (which also indicates a lower degree of liquid-phase backmixing) to maximize the distillate yields and reduce coking. The physicochemical properties of the coke formed were also found to vary according to the feed type, e.g., the thermal conductivity of the coke produced from naphtha and gas oil cracking ranges in \(3.5–5.8\ \text{W m}^{-1} \text{°C}^{-1}\), while that...
of those produced from ethane or LPG cracking ranges in 11.6–14 W m\(^{-1}\) °C\(^{-1}\).\(^{64}\)

### 4.2. Kinetics
Thermal cracking reactions have been found to follow zero-order to first-order kinetics\(^ {36}\) and an Arrhenius-type relationship:

\[
k = A \exp(-E/RT) \tag{16}
\]

The activation energy of cracking and coke formation can range from 22 to 83 kcal/mol.\(^ {36}\) The activation energy \(E\) in eq 16 can be assumed to be 50 kcal/mol, which is the thermal cracking energy for C\(_{15}\) compound.\(^ {57}\)

The residue comprises a large number of complex organic components, and a detailed kinetic model involving the cracking behavior of each of the components is impractical. Hence, the pseudo-components (also termed as lump) are considered by group contribution method, based on their physicochemical properties such as boiling point, solubility, carbon number, etc. On the basis of the thermal property variation (mostly boiling point) in these components, lumped kinetic models have been proposed (Table 3). The cited models can be categorized into (i) parallel reaction models and (ii) parallel–consecutive reaction models.

The parallel reactions models\(^ {28,31,65}\) consider the thermal cracking of the feed without further cracking of the products or the compositional changes within the feed. Castellanos et al.\(^ {66}\) divided the heavy oil into a large number of model components based on the carbon number and considered thermal cracking of each component into lower carbon number and olefinic component, while Benito et al.\(^ {33}\) and Xiao et al.\(^ {67}\) reported parallel decomposition of residue to distillates and coke. A detailed investigation pertaining to the product yields of the visbreaking process and their properties prediction has been reported by Dente et al.\(^ {14}\) The authors have proposed a mechanistic approach that elucidates the fouling of the coils, physicochemical properties of the products viz. residue stability, sulfur and asphaltenes content, viscosity, specific gravity, etc.

The parallel–consecutive model considers sequential cracking of product species as well. The lumped model by Takatsuka et al.\(^ {68}\) predicts variation in the yields of the distillates formed, along with the compositional changes of the feed. The model proposed by Del Bianco et al.\(^ {32}\) for predicting the thermal behavior of Belaym VR showed coke formation through secondary reactions of the intermediates, while models reported by Yasar et al.\(^ {34}\) Xiao et al.\(^ {67}\) and Trauth et al.\(^ {69}\) deal with the interconversion of the solubility class of components and their rate parameters. Recently, Kataria et al.\(^ {38}\) reported the variation in the yield of pseudo-components (based on their boiling point), the activation energies, and the cracking as a function of feed properties by employing a five-lump and seven-parameter model.

### 5. Visbreaker Designs

#### 5.1. Coil Visbreaker
The coil visbreaker is operated at high temperature and low residence time and, thus, is also termed as a high-temperature, short-residence-time (HTST) process. Foster Wheeler has been at the forefront of designing the heaters for the coil-visbreaking process. In coil visbreaking, the visbreaker feed from the preheater enters the furnace at 300–330 °C and undergoes thermal cracking in the coil in the temperature range of 460–480 °C for the duration of 2–5 min. Steam (\(\sim 1\) wt %) is injected along with the feed to (i) generate the turbulence and, hence, increase the heat transfer coefficient at the wall, (ii) control the liquid-phase residence time, and (iii) prevent the coking along the tube walls. The cracking reactions (C–C cracking) occur in the liquid phase and are slightly endothermic (192 kcal kg\(^{-1}\) of the product boiling below 204 °C).\(^ {70}\) The cracked feed at the coil outlet is immediately quenched (up to 350 °C) (Figure 5A) using fractionator bottoms and is then distilled into different boiling cuts.

Variations in the temperature, pressure, and conversion along the reactor length for the coil-type visbreaker operation are shown in Figure 5B.\(^ {43}\) The coil-inlet pressure (~2.5 MPa) is maintained at higher values so as to facilitate the transport of the feed. The pressure drop (~1.7 MPa) along the reactor length is mainly due to the two-phase frictional pressure drop. The gas phase initially consists mainly of the steam. However, along the length, the gas-phase fraction increases because of partial vaporization and thermal cracking of the feed. The temperature of the feed increases continuously along the coil length; however, because of the onset of cracking and the endothermic nature of the reactions, the rate of temperature rise reduces slightly after a certain coil length.

The cracked products obtained vary from gas (C\(_1\)–C\(_4\)) to gas oil. The products, viz. gas, gasoline, and, to a smaller extent, gas oil, are separated in a fractionator. However, the extent of permissible conversion and the subsequent withdrawal of distillates are governed by the stability, CCR, viscosity, and pour point of the visbroken residue. The insoluble content (hot filtration test), heated tube fouling, xylene equivalent, Shell P-value, and Merit number tests are used to ensure the stability of the fuel oil.\(^ {71–73}\) The nature of the cutter stock, recycle oil, or lube-oil extract that are used to blend and meet the desired viscosity specifications also affect, to some extent, the final stability of the fuel oil.

In order to improve the throughput of the process, the single-coil-type process was modified to two-coil-type. In the coil-visbreaking process, the heater outlet temperature (about 480 °C) is considerably higher than in the soaker visbreaking process (about 450 °C). As a consequence, the clean tube-wall temperature and the fluid-film temperature are correspondingly higher. The higher tube-wall temperature leads to the coke buildup at the wall. As a consequence, the tube wall becomes hotter in order to overcome the thermal resistance of the coke until the maximum allowable tube-wall temperature is reached.\(^ {74}\) The precipitated asphaltenes and the coke formed get deposited on the heater tube surface, thereby increasing heater duties and pressure drop, which results in untimely shutdown of the unit.

#### 5.2. Coil-Soaker Visbreaker
In coil-soaker operation, feed is allowed to pass through the coil and is kept at relatively lower temperature and the residence time (~450 °C, 2–3 min) followed by soaking is held for a longer time (15–25 min) in an adiabatic hollow drum known as a “soaker”. The reduction in the coil temperature and simultaneous increase in the residence time in the soaker give similar conversions as in the case of the coil type. Thus, the coil-soaker type is described as the low-temperature, high-residence-time (LTHT) route. The technology has been developed by Shell and is also known as Shell soaker visbreaking process (SSVP). The first of the Shell soaker visbreakers went on stream in 1962 in Curacao, Netherland Antilles.\(^ {74}\) The process flow diagram (Figure 6A) for the coil-soaker type shows that the feed from the coil outlet follows the additional soaker drum path in an upflow manner and is quenched (using appropriate cutter stock) at the soaker outlet before fractionation.

The variation in the temperature, pressure, and conversion in the case of the coil-soaker type is shown in Figure 6B.\(^ {43}\) The feed cracking occurs both in the coil and in the soaker. The pressure at the soaker inlet is about 1.3 MPa and reduces
### Table 3. Summary of the Reported Work on Visbreaking Kinetics

<table>
<thead>
<tr>
<th>Author</th>
<th>Feed</th>
<th>Exp Details</th>
<th>Model</th>
<th>Conclusions</th>
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<tr>
<td></td>
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<td><strong>Parallel Models</strong></td>
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<tr>
<td>Al-Soufi et al.</td>
<td>Heavy</td>
<td>Reactor T (°C) 435-480</td>
<td>Pilot plant Coal-Solvent type Cracked products (350°C-)</td>
<td>1. Within the severity range covered, thermal cracking follows first-order. 2. E = 23.7 kcal mol⁻¹</td>
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<td></td>
<td>[Iraq] residue (350°C, 75°C, 15°C)</td>
<td>RT (min) 0.7-1.8</td>
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<td>P (MPa) Solvent 2.5-6.3 0.7</td>
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<td>Feed Cracked products (350°C-)</td>
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<tr>
<td>Krishna et al.</td>
<td>Aghajani long residue (370°C, 33°C, CR=7.8)</td>
<td>Reactor Dimensions T (°C) Flow rate (bph) P (MPa)</td>
<td>Bench scale unit (60 m³)</td>
<td>1. Within the severity range covered, thermal cracking follows first order. E = 53.4 kcal mol⁻¹. A = 2.17 x 10⁶ s⁻¹. 2. Secondary cracking of the products starts beyond 7% conversion.</td>
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<td>Castellan et al.</td>
<td>Maya &amp; Arizmendi AR, VR</td>
<td>Reactor Industrial Duhb’s Unit</td>
<td></td>
<td>1. Under industrial operating conditions, feed follows first-order thermal cracking. 2. The model predicts the yields of industrial units and has been used successfully for design purpose.</td>
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<td>Di Carlo and Janis</td>
<td>Rospi di mare, Belaym, Eis Sider</td>
<td>Reactor T (°C)</td>
<td>Pilot plant (coal type)</td>
<td>AR k → R</td>
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<tr>
<td></td>
<td>residue</td>
<td></td>
<td>455-500</td>
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<tr>
<td>Benito et al.</td>
<td>Asphaltic</td>
<td>Reactor T (°C)</td>
<td>Steel tubular reactor Dimensions T (°C)</td>
<td>H-Residue</td>
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<td>Length 45 mm</td>
<td>I-lighter oil</td>
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<td>425-475</td>
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<td>5-40</td>
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<tr>
<td>Xia et al.</td>
<td>Heavy oil</td>
<td>Reactor T (°C)</td>
<td>Micro-reactor</td>
<td>400-500</td>
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<td><strong>Parallel consecutive models</strong></td>
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<tr>
<td>Takatsu-ka et al.</td>
<td>Residual oil</td>
<td>Reactor T (°C)</td>
<td>Flow reactor, Semi-batch, autoclave 400-480</td>
<td>1. Atmospheric equivalent temperature and hydrocarbon partial (HC) pressure were incorporated to estimate Arrhenius rate parameters. The reaction model was found to represent the degree of cracking over a wide range of operating conditions. 2. Higher HC partial pressure decreases the reaction rate of polycondensation reactions; while degree of cracking increases with increasing reactor pressure. 3. Polycondensation reactions that proceed via consecutive reaction mechanism are greatly affected by RTD to yield higher content of quinoline insoluble pitch in product. 4. The estimated values of activation energy for cracking reactions were found to be 60 kcal mol⁻¹ while 46-50 kcal mol⁻¹ for polycondensation reactions.</td>
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<td>0.450</td>
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<tr>
<td>Del Bianco et al.</td>
<td>Belayo vacuum residue (20.8 wt %)</td>
<td>Reactor T (°C)</td>
<td>Batch Reactor 400-450</td>
<td>1. Coke is formed via some intermediate. 2. E = 40.4 kcal mol⁻¹; A = 31.97 atm⁻¹; E = 33.9 kcal mol⁻¹; A = 40.92 min⁻¹. 3. Gas composition remained unchanged for the conversion. 4. Structural study shows thermal cracking of asphaltenes follows dehydration reactions. 5. Condensation reaction prevails at high severity levels.</td>
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<td>RT (min) 0-120</td>
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<td>P (MPa) 1 (N₂ atm)</td>
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<tr>
<td>Trauth et al.</td>
<td>Honda, Maya, Arab Light, Arabian Heavy residue &amp; their isolated asphaltenes</td>
<td>Reactor T (°C)</td>
<td>Thin walled glass tube 400-450</td>
<td>1. The reactivity was found to be proportional to the asphaltene content and their aromacity and thus HR &gt; AlIFR &gt; MR &gt; ALR. 2. The kinetic parameters were estimated for residues and isolated asphaltenes and the activation energy of HR and ALR, were found to be higher than their respective isolated asphaltenes for all the reaction pathways.</td>
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<td>RT (min) 20-180</td>
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<td>P (MPa) 0.5 (N₂ atm)</td>
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<tr>
<td>Kafta et al.</td>
<td>RHE, NSR, AMR, VR Feed</td>
<td>Reactor T (°C)</td>
<td>Batch Reactor 400-450</td>
<td>1. Gas, Gasoline, LGO were found to be stable products under the studied severity while VGO was found to undergo further cracking. 2. The crackability of VR was found to be higher vis-à-vis their asphaltenes. 3. Activation energy for the decomposition of VR and formation of distillates were found to be a function of feed properties.</td>
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<td>RT (min) 0-15</td>
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<td></td>
<td>P (MPa) 1.2 (N₂ atm)</td>
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slightly due to the hydrostatic head, cracking, and vaporization. The temperature in the soaker reduces axially due to the endothermic nature of the cracking reactions (∼10–20 °C). It may be pointed out that, because of the lower temperatures and the low conversion in the heater in soaker visbreaking, the coke buildup is much slower, so that the tube-wall temperature increase is slower by a factor of about 3, as has been found in operating plants. The soaker drum can be considered similar to a bubble-column reactor in which the gas phase consists of product gas, vaporized low-boiling components, and the added turbulizing steam. The RTD and tomographic experiments have shown that the average gas holdup ranges from 20–40% with bubble size ranging from 3–15 mm. Further, the study also revealed that the residence time of the gas phase is around 1/10 of the residence time of the liquid phase, and thus, the overall conversion may be assumed to be controlled by the liquid-phase cracking only.

The advantages of the coil-soaker process over the coil process can be summarized as follows:

1. The soaker drum allows the heater to operate at a lower outlet temperature by providing the residence time required to achieve the desired reaction. Because of the lower heater-outlet temperature, the heater duty and, in turn, the fuel consumption is only 70% of that for the coil-visbreaking process.

2. The lower fuel consumption reduces the generation of large amounts of waste heat steam. Earlier, these steam quantities were a significant part of the visbreaking process and quite often upset the refinery steam balance.

3. It is known that the activation energy required for the cracking of the hydrocarbons is inversely proportional to their carbon number; it is higher for low carbon number compound and vice versa. This implies that the selectivity to the cracking of the feed in the coil-soaker mode, due to their relatively lower temperature vis-à-vis the coil type, allows only the cracking of higher molecules, and already-cracked molecules remain unaffected.

4. The lower temperature results in less coke formation and less destabilization of the feed, enhancing the unit run length typically from about 3–6 months (in the case of the coil type) to about 18 months.

5. The low operating temperature results in low operating cost.

5.3. Soaker with Internals. Figure 7A shows a typical representation of a soaker. As mentioned earlier, a soaker is essentially a bubble column where the volumetric coefficient increases from bottom to top. The gas phase is in the form of bubbles in a wide size distribution. The column operates in the heterogeneous regime where the concentration of gas phase varies in the radial as well as axial directions. At this stage, it may be noted that, in the homogeneous regime, the bubble concentration is uniform in both radial and axial directions. The extent of uniformity of gas bubbles has direct repercussions on the performance of bubble columns. For instance, the radial and axial nonuniformity in the gas phase (holdup and bubble-size distribution) results in gross liquid circulation with an upflow in the central region and downflow in the near-wall region. The liquid circulation velocity is given by the following equation:
\[
V_C = 1.31 \left[ \frac{gD_C}{\epsilon_G} \left( V_G - \frac{\epsilon_G}{1 - \epsilon_G} V_L - \epsilon_G V_B \right) \right]^{1/3}
\]  

(17)

The circulation velocities are of the order of 0.3–3 m/s and as a result of such an intense liquid circulation, the liquid phase remains completely backmixed. Quantitatively, the liquid-phase dispersion coefficient is given by

\[
D_L = 0.31D(V_C + V_L)
\]  

(18)

The heterogeneity of the gas phase also reduces the gas-phase residence time as compared to that in the homogeneous regime. The above phenomenon leads to a wide spread in the gas- and liquid-phase residence times and affects visbroken residue stability and mid-distillate selectivity. The direct and obvious effect is the reduction in the intense concentration gradients, resulting in decreased overall conversion. Also, the overcracking of the feed due to backmixing and dead zones causes decreased solubility of asphaltenes resulting in their early precipitation, thereby producing an unstable fuel oil. In some cases, decreased selectivity toward mid-distillates and deteriorated stability have also been reported.77

The above discussion suggests that the performance of the soaker can be improved by reducing the extent of backmixing in the liquid phase. Since the major reason for backmixing is the gross liquid circulation (eqs 17 and 18), in practice, the backmixing is reduced by reducing (in an extreme case, by arresting) the liquid circulation. This is achieved by sectionalization (Figure 7B) with sieve plates, radial baffles, etc. Some of the designs77–80 are shown in Figure 8. Recently, Kumar et al.,81 using RTD experiments for a visbreaker pilot plant with and without a sectionalized soaker drum (4L volume) by perforated plates, concluded that the sectionalized soaker offers several advantages, which are as follows: (i) reduction in backmixing (by 3–5 times); (ii) increased LPG + gasoline, gas oil, and distillate yield by 10–16%, 11–19%, and 1–17%, respectively, under an identical temperature gradient; and (iii) better fuel oil stability.

5.4. High-Conversion Soaker Cracker. The high-conversion soaker cracking (HSC) process developed by Toyo Engineering Corporation (TEC) and Mitsui Kozan Chemicals Ltd. enhances the conversion of the VR to low-boiling products.82 The feed for the HSC process includes the refractory bottoms of the visbreaker unit or the vacuum-distillation unit and involves the continuous thermal cracking reactions with simultaneous deep steam stripping in the countercurrent manner, i.e., the feed moving from the soaker head and steam moving from the bottom. Feedstock is heated to temperatures of 440–460 °C, depending on the desired conversion in the soaker drum. Typically, low pressure (≈ 0.1 MPa) and high feed velocities are chosen as the operational and design variables to prevent coking on the heater tubes. These features differentiate it from the soaker used in the conventional visbreaking process. The liquid product (C5, 520 °C) yield of the HSC process is about 44 wt %.82 HSC can be integrated with the existing coil-visbreaking unit for higher conversions and simultaneously allows the use of the visbroken residue (without the addition of the cutter stock) as a fuel oil. The authors have also suggested

Figure 8. Different configurations of proposed soaker internals.
coupling of the HSC process with the ROSE process (supercritical solvent extraction) for enhanced recovery of the liquid products along with the deasphalted oil.

6. Design Considerations

6.1. Estimation of Design Parameters. In the visbreaking soaker drum, steam, product gas (C₃—heptane), and low-boiling hydrocarbons (typically boiling point (bp) < 350 °C) act together as the dispersed gas phase while the liquid (typically bp > 350 °C) forms the continuous phase. Fractional gas holdup is an important design parameter, which determines the effective volume of the reactor available for the liquid-phase thermal cracking reactions. The single-stage flash calculations (ASPEN Plus software version 10.2) for different vacuum residues under cracking reactions. The single-stage flash calculations (ASPEN Plus software version 10.2) for different vacuum residues under cracking reactions. The single-stage flash calculations (ASPEN Plus software version 10.2) for different vacuum residues under cracking reactions. The single-stage flash calculations (ASPEN Plus software version 10.2) for different vacuum residues under cracking reactions. The single-stage flash calculations (ASPEN Plus software version 10.2) for different vacuum residues under cracking reactions. The single-stage flash calculations (ASPEN Plus software version 10.2) for different vacuum residues under cracking reactions.

4. On the basis of these comprehensive studies, a brief review pertaining to the effect of gas density and pressure on the products along with the deasphalted oil.

4.1. Gas Holdup in High-Pressure Bubble Column. A systematic investigation of gas holdup structure in bubble columns has been reviewed by Joshi et al. The studies pertaining to the effect of gas density and pressure on the average gas holdup in a bubble column are summarized in Table 4. On the basis of these comprehensive studies, a brief review has been given below.

The gas holdup was found to increase with an increase in the operating pressure. This effect of pressure has been attributed to the vapor compression leading to the increase in the gas density, which increases the gas-phase momentum. Therefore, at the gas distributor, because of the higher upward force of the gas, the bubbles detach in their earlier growth stage, resulting in reduction in their size.

The Kelvin–Helmholtz stability analysis reveals that the pressure mainly affects the stability of large bubbles, which tend to break because of the growth of surface instability, correspondingly reducing the maximum stable bubble size, \( d_{\text{b,max}} \). As a result, the bubble-size distribution becomes narrower and their rise velocities are reduced, resulting in the shift of the regime transition point to higher superficial transition velocities, \( V_{\text{trans}} \), of the vapor phase.

The variation in the interfacial fluid properties as a result of elevated pressure was found to affect the bubble formation, bubble coalescence, and bubble breakup rates. The bubbles during their passage undergo frequent coalescence that involves (a) the approach of two bubbles to form a thin liquid film between them, (b) the thinning of the liquid film by the drainage of the liquid under the influence of gravity and suction due to capillary forces, and (c) the rupture of the film at critical thickness.

Lin et al. found that increasing the pressure reduces the surface tension and increases the liquid viscosity and surface drag, \( \phi \) (the parameter defined as the velocity gradient at the surface due to the adsorbed layer of the gas), which decreases the film-thinning velocity, thereby reducing the bubble-coalescence rate. Further, the reduction in maximum stable bubble size, \( d_{\text{b,max}} \), occurs as a result of a decrease in the gas–liquid surface tension and an increase in the gas density at elevated pressure. As a consequence of these phenomena, higher gas holdup was observed at higher pressure.

The radial gas holdup profile is given by

\[
e_{G}(r) = \frac{m}{m} + \frac{2}{m} e_{G}(1 - (r/R)^{m})
\]

At atmospheric pressure, the radial gas holdup profile was found to be parabolic, i.e., holdup profile index, \( m \), varied from 3.6 to 2.0 with increasing \( V_{G} \) from 20 to 180 mm/s, respectively. However, with increasing the pressure from 0.1 to 0.7 MPa, \( m \) value increased from 3.6 to 5.4 at \( V_{G} = 20 \text{ mm s}^{-1} \) and from 2.0 to 3.0 at \( V_{G} = 180 \text{ mm s}^{-1} \), indicating flattening of the holdup profiles.

The above effects are relatively more significant for the case of the perforated-plate sparger than that of the sintered-plate sparger. Studies with porous plates as gas distributors show a much smaller or no influence of pressure at low superficial gas velocities on the gas holdup. It has been reported that gas bubbles formed from a porous plate show much interaction with each other on the surface of the porous plate, leading to coalescence of the bubbles. This in turn was found to have partial or total disguise of the effect of pressure on the bubble-formation process and, thus, on the gas holdup. Moreover, the magnitude of the pressure in the case of noncoalescing liquids was found to be higher than that for coalescing liquids at elevated pressures for identical design and operating conditions.

Wilkinson et al., Reilly et al., Letzel et al., Krishna et al., and Yang and Fan have described the influence of gas density on the regime of operation. Experimental analysis showed that the increased gas density stabilized the regime of homogeneous bubble flow and, consequently, delayed the transition to the churn–turbulent flow regime. Thus, the transition superficial gas velocity was found to be a unique function of the gas density. Moreover, Wilkinson et al. reported that the gas holdup is virtually independent of the column diameter above 0.15 m, column height-to-diameter ratio in excess of 5, and sparger hole diameter larger than 2 mm.

An insignificant effect of superficial liquid velocity on the gas holdup at elevated pressures has been reported by Yang and Fan, indicating that the net liquid motion is negligible as compared with the bulk liquid motion and, hence, has little effect on bubble characteristics. The influence of elevated pressure on the gas holdup for low- and high-viscous systems has been reported by Urseanu et al. For the low-viscous system, increasing the pressure of the system resulted in the expansion of the dense/gas phase. Therefore, overall holdup was found to increase considerably. However, for high-viscous systems, the effect shown by high-pressure operation was less prominent, since the dense/gas phase was almost inextensible at low gas velocities, resulting in a less prominent effect of pressure on overall gas holdup.

Gandhi et al. have analyzed all the published data over the range 0.045 ≤ \( D \) ≤ 5.5 m, 0.0003 ≤ \( V_{G} \) ≤ 0.72 m/s, 100 ≤ \( P \) ≤ 15600 kPa, and 284 ≤ \( T \) ≤ 538 K. They have developed a predictive procedure using support vector machines.

6.1.2. Gas Holdup in Sectionalized Bubble Column. It has been mentioned earlier that the value of \( e_{G} \) increases along the
<table>
<thead>
<tr>
<th>Author(s)</th>
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<th>Geometrical details</th>
<th>Operating variables</th>
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</tr>
</thead>
</table>
| Tarny et al.         | $\text{N}_2$-water heptane coal liquid (continuous) | $D_{cv} = 0.024-0.61$ m $L = 1.2-8.5$ m sparger = single and multiple nozzle, bubble cap | $V_G = 0.006-0.23$ m s$^{-1}$ | 1. Increasing the pressure delayed the regime transition  
2. Significant increase in $\varepsilon_G$ with increase in gas density  
3. At high pressure, $D_a$ values were 2.5 times smaller than those observed at atmospheric conditions  
4. The high $\varepsilon_G$ values were attributable to the reduced bubble coalescence  
5. Two distinct regimes of operation were observed, with lower half of column in the bubbly regime while the upper half showed churn turbulent regime over studied $V_G$  
6. The homogeneous regime showed 40% higher $\varepsilon_G$ than churn turbulent region  
7. The addition of solids increased bubble coalescence and reduced $\varepsilon_G$ |
| Clark                | $\text{N}_2$-water methanol (semibatch) | $D_{cv} = 0.075$ m $L = 3$ m sparger = sintered metal distributor $d_f = 90$ µm | $V_G = 0-0.06$ m s$^{-1}$ | 1. $\varepsilon_G$ increased with pressure both for water and aqueous DEA solution  
2. Relative increase in $\varepsilon_G$ was found smaller than with aqueous DEA solution  
3. The reduced effect of pressure on $\varepsilon_G$ observed in the case of porous plate was due to the bubble coalescence in the vicinity of the distributor surface  
4. The interfacial area, $a$, increased with increase in pressure, and relative increase in $a$ was smaller at lower $V_G$ |
| Oyevaar et al.       | $\text{N}_2$-aqueous DEA solution + antifoaming agent (semibatch) | $D_{cv} = 0.081$ m sparger = perforated plate, $d_0 = 0.4$ mm, sintered plate $d_f = 30$ and 100 µm | $V_G = 0.01-0.10$ m s$^{-1}$ | 1. Increasing the pressure delayed the regime transition  
2. $V_{ran}$ was found to be a unique function of gas density and liquid properties  
3. In churn turbulent regime, the higher values of $\varepsilon_G$ were attributed to bimodal bubble-size distribution  
4. The column dimensions had negligible effect on $\varepsilon_G$ when $D_c \geq 0.15$ m, $L/D_c > 5$, $d_0 > 2$ mm |
| Krishna et al.       | $\text{N}_2$, He, CO$_2$, Ar, SF$_6$ deionized water, monoethylene glycol, n-butanol, turpentine (semibatch) | $D_{cv} = 0.16, 0.19$ m $L = 1.2, 4$ m sparger = ring type, $d_0 = 2$ mm, $n = 37$ $d_f = 10$ mm, $n = 19$ | $V_G = 0.02-0.18$ m s$^{-1}$ | 1. Increasing the pressure delayed the regime transition  
2. $V_{ran}$ was found to be a unique function of gas density and liquid properties  
3. In churn turbulent regime, the higher values of $\varepsilon_G$ were attributed to bimodal bubble-size distribution  
4. The column dimensions had negligible effect on $\varepsilon_G$ when $D_c \geq 0.15$ m, $L/D_c > 5$, $d_0 > 2$ mm |
| Wilkinson et al.     | $\text{N}_2$, He, CO$_2$, Ar, SF$_6$ $n$-heptane, monoethylene glycol, water (semibatch) | $D_{cv} = 0.16, 0.23$ m $L = 1.2$ m sparger = ring type, $d_0 = 2$ mm, $n = 37$ $d_f = 10$ mm, $n = 19$ | $V_G = 0.006-0.2$ m s$^{-1}$ | 1. Increasing the pressure delayed the regime transition  
2. $V_{ran}$ was found to be a unique function of gas density and liquid properties  
3. In churn turbulent regime, the higher values of $\varepsilon_G$ were attributed to bimodal bubble-size distribution  
4. The column dimensions had negligible effect on $\varepsilon_G$ when $D_c \geq 0.15$ m, $L/D_c > 5$, $d_0 > 2$ mm |
| Reilly et al.        | $\text{N}_2$, He, air, CO$_2$ ISOPAR G, ISOPAR M, TCE, Varsoil DX 3139, water (semibatch) | $D_{cv} = 0.15, 0.23$ m $H = 1.2$ m X-type sparger $d_0 = 0.5$ mm, $n = 64$ | $V_G = 0.006-0.23$ m s$^{-1}$ | 1. Increasing the gas density increased the stability of the bubbly flow regime and $V_{ran}$  
2. In the case of the homogeneous regime, $\varepsilon_G \propto M$, and for the heterogeneous regime, $\varepsilon_G \propto M^{0.45}$, where $M$ = specific gas-phase momentum given as $M = \rho V_G (1 - \varepsilon_G)$ |
| Luo et al.           | $\text{N}_2$-Paratherm-solids (continuous) | $D_{cv} = 0.058$ m $L = 0.8$ m sparger = perforated plate $d_0 = 2.4$ mm, $n = 37$ square pitch $d_f = 2.1$ and 3 mm | $V_G = 0.006-0.23$ m s$^{-1}$ | 1. The average bubble size decreases and the bubble-size distribution becomes narrower with an increase in pressure  
2. The effect of pressure on regime transition was found significant up to 6 MPa  
3. Decrease in $d_b$, reduced bubble-size distribution, and bubble-rise velocity contributed to increased $\varepsilon_G$ with increasing pressure  
4. An increase in gas-phase momentum and the decrease in the surface tension, as a result of increase in pressure, increased $\varepsilon_G$ while the increase in liquid viscosity decreased $\varepsilon_G$  
5. An increase in the temperature increased $\varepsilon_G$  
6. Increase in the pressure delayed the regime transition and decreased the rise velocity, $V_b$, of large gas bubbles  
7. The rise velocity of large bubbles was found to be inversely proportional to the square root of gas density |
| Lin et al.           | $\text{N}_2$-Paratherm (semibatch) | $D_{cv} = 0.0508, 0.10$ m $L = 0.8, 1.58$ m sparger = ring type $d_0 = 3$ mm | $V_G = 0-0.3$ m s$^{-1}$ | 1. Increasing the pressure delayed the regime transition  
2. Significant increase in $\varepsilon_G$ with increase in gas density  
3. At high pressure, $D_a$ values were 2.5 times smaller than those observed at atmospheric conditions  
4. The high $\varepsilon_G$ values were attributable to the reduced bubble coalescence  
5. Two distinct regimes of operation were observed, with lower half of column in the bubbly regime while the upper half showed churn turbulent regime over studied $V_G$  
6. The homogeneous regime showed 40% higher $\varepsilon_G$ than churn turbulent region  
7. The addition of solids increased bubble coalescence and reduced $\varepsilon_G$ |
| Letzel et al.        | $\text{N}_2$-deionized water (semibatch) | $D_{cv} = 0.15$ m $H = 1.22$ m sparger = perforated plate $d_0 = 0.5$ mm, $n = 200$ | $V_G = 0-0.4$ m s$^{-1}$ | 1. Increasing the pressure delayed the regime transition  
2. Significant increase in $\varepsilon_G$ with increase in gas density  
3. At high pressure, $D_a$ values were 2.5 times smaller than those observed at atmospheric conditions  
4. The high $\varepsilon_G$ values were attributable to the reduced bubble coalescence  
5. Two distinct regimes of operation were observed, with lower half of column in the bubbly regime while the upper half showed churn turbulent regime over studied $V_G$  
6. The homogeneous regime showed 40% higher $\varepsilon_G$ than churn turbulent region  
7. The addition of solids increased bubble coalescence and reduced $\varepsilon_G$ |
length of the column because of the formation of the gaseous products. The gas holdup has direct and indirect implications. Directly, it decides the fraction of the liquid phase and, hence, the reactor volume available for the visbreaking reactions. Indirectly, the value of εG is not uniform even in the radial direction. Because of this, pressure gradients are created in the radial direction, which, in turn, generates intense liquid circulation in the soaker. The resulting liquid circulation time is an order of magnitude lower than the residence time, and hence, the liquid phase tends to be completely backmixed. Thus, in order to reduce the intensity of the effects of the radial and the axial profiles of εG, sectionalization is beneficial. The role of sectionalization on the liquid phase is discussed in Section 6.1.4, and the effect of liquid-phase mixing on the visbreaking reaction is described in Section 6.2.2.

In the sectionalized soaker, the overall gas holdup is affected by the geometry of the internals, the process severity, and the mode of operation. The investigations with regard to the gas holdup in a sectionalized bubble column are summarized in Table 5. The research efforts presented by different investigators are summarized below.

In a multistage bubble column, each section acts as a sparger-dominated region where the bubble size is primarily governed by the hole diameter of the partitioning plate. The higher gas holdup observed in these reactors is possibly due to the reduction in the liquid-phase circulation velocities within the stage. In addition, higher energy dissipation across the perforated trays results in the redistribution of gas bubbles, thereby reducing the overall bubble size. Therefore, an increase in the bubble residence time, a smaller average bubble diameter, and a decreased bubble-coalescence rate together contribute to a higher average gas holdup. For the same percent free area, the gas holdup was found to increase with decreasing the hole diameter, while for the same hole diameter, increasing the percent free area of the sectionalizing plate was found to decrease the overall gas holdup. The formation of gas pockets below the trays was also found to contribute to the overall gas holdup when VG > 0.03 m s⁻¹. However, this effect was found to be insignificant when the column diameter exceeds 0.38 m. The partitioning-plate hole diameter was found to show a more prominent effect on the gas holdup than the percent free area of the sieve plate. In contradictory results, Kemoun et al. found that the overall gas holdup remained identical for tray and simple bubble columns; however, the radial density gradients (ΔεG) were found to decrease by incorporating the internals. The average gas holdup showed a weak dependency on the liquid superficial velocity and the geometry of the gas distributor.

6.1.3. Liquid-Phase Mixing and Axial Mixing in High-Pressure Bubble Column. Soaker technology offers advantages of lower heater duties, lower capital investment, increased run lengths, and low susceptibility to operational upsets. However, the liquid-phase backmixing occurring in the soaker often diminishes the process performance. The detrimental effect arising because of backmixing causes over-cracking of the residue, which affects the fuel oil stability and reduce the selectivity toward middle distillates.

Table 4. Continued

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<thead>
<tr>
<th>author</th>
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<th>geometrical details</th>
<th>operating variables</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Yang and Fan</td>
<td>N2—water</td>
<td>DC = 0.051, 0.10 m</td>
<td>VG = 0–0.4 m s⁻¹</td>
<td>1. Effect of liquid velocity on εG was found to be insignificant</td>
</tr>
<tr>
<td></td>
<td>N2—Paratherm</td>
<td>H = 0.56, 0.92 m</td>
<td>VG = 0–0.01 m s⁻¹</td>
<td>2. Axial dispersion coefficient decreased with an increase in the pressure</td>
</tr>
<tr>
<td></td>
<td>(continuous)</td>
<td>sparger = perforated</td>
<td>P = 0.1–10.3 MPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>plate d0 = 1.5 mm, n = 120</td>
<td>μL = 0.028 Pa s</td>
<td></td>
</tr>
</tbody>
</table>

The liquid- and gas-phase backmixing have been extensively investigated in the literature. However, it may be pointed out that most of the studies have been carried out at atmospheric pressure and especially for the air—water system, whereas the investigations under high-pressure conditions are very scarce. Holcombe et al. determined the axial liquid dispersion coefficient in a 78 mm bubble column with 1.8 m height and a pressure range 0.3–0.72 MPa. The superficial gas velocity was varied up to 0.6 m/s. They used heat as a tracer to measure the thermal dispersion coefficient. The authors found that the effect of pressure on thermal dispersion coefficient is negligible in the pressure range of their study.

Tarmy et al. investigated liquid-phase axial mixing in industrial coal liquefaction reactors using radioactive tracers. The operating pressure was varied up to 17 MPa. They found that the values of dispersion coefficient increased with an increase in pressure.

Houzelot et al. investigated the axial dispersion in a 50 mm i.d. column. The superficial gas velocity was varied up to 6 mm/s, and pressure was varied in the range of 0.1–0.3 MPa. They have observed an insignificant effect of pressure on the axial dispersion coefficient, which is perhaps due to the limited range of variables covered in their work.

Wilkinson et al. measured the axial dispersion coefficient in a batch-type 158 mm i.d. bubble column with nitrogen—water system at pressures between 0.1 and 1.5 MPa using the electrical conductivity method. It was found that the value of Dk increases with increasing pressure, especially under high gas velocity conditions (VG > 100 mm/s).

Yang and Fan measured liquid axial dispersion coefficient at high pressure (up to 10.3 MPa) in 50.8 and 101.6 mm i.d. bubble columns. The superficial liquid and gas velocities were varied in the range of 3.4–10 and 20–400 mm/s, respectively. They have used heat as a tracer to measure the thermal dispersion coefficient. They have found that the axial dispersion coefficient decreases with an increase in pressure. Further, they have also observed that the distributor design does not have a significant effect on the liquid-phase mixing.

From the foregoing discussion, it is clear that contrasting observations have been made, and these have not been rationalized in a systematic manner on the basis of well-understood fluid mechanics in bubble columns. The prevailing unsatisfactory state of the art is principally because of the following reasons:

(1) The most common approach to account for the nonideality has been based on a one-dimensional (1-D) axial-dispersion model (ADM). Because of its simplicity and ease of use, the ADM has remained popular in reactor design, and numerous correlations for the axial liquid-dispersion coefficient in bubble columns have been developed over the years. However, the ADM makes an attempt to cover all the types of nonidealities without including the understanding of the detailed fluid mechanics behind each nonideality.

(2) Most of the experiments have selected air—water as the gas—liquid system. The results with organic liquids at higher temperatures and pressures have been contradicting. For instance, Wilkinson et al. and Panvelkar et al. have observed an increase in axial-dispersion coefficient (Dk) with an increase...
in pressure. However, Yang and Fan\textsuperscript{97} reported exactly the reverse. In order to rationalize the above-mentioned apparent discrepancies, Lorenz et al.\textsuperscript{115} performed a detailed computational fluid dynamics (CFD) simulation of flow pattern and axial mixing. A brief summary is given below:

The flow pattern depends upon the superficial gas velocity ($V_g$), the column diameter ($D$), and the nature of the gas–liquid system. The simulations have been carried out for three different gas–liquid (N$_2$–water, N$_2$–ethanol, and N$_2$–1-butanol) systems, for two different temperatures (298 and 323 K), and for two different pressures (0.1 and 0.5 MPa). The CFD simulations show that, in the presence of ethanol, the values of $V_g$ are lower ($C_l = 0.251$) and the fractional gas holdup values (0.205) are higher than the corresponding values for the N$_2$–water system (0.319 and 0.174). Further, the holdup profile is flatter ($C_0 = 2.22$) than that in the N$_2$–water system ($C_0 = 2.37$). Therefore, the liquid circulation velocities are lower in the presence of ethanol (Figure 9). The same effect can be seen for the N$_2$–1-butanol system. The holdup profile is flatter ($C_0 = 1.99$) as compared to that for the N$_2$–water system.

With regard to the temperature, it has been shown that, as the temperature increases from 298 to 323 K, the liquid velocity and holdup increase at a constant pressure of 0.1 MPa. The CFD simulations have shown that the value of $V_g$ is higher ($C_l = 0.319$) and the fractional gas holdup (0.174) is lower at a temperature of 298 K than the values of $V_g$ and fractional gas holdup at 323 K (0.285 and 0.195, respectively). Similar observations have been made for the other three different gas–liquid systems.

Further, as the pressure increases from 0.1 to 0.5 MPa, the liquid circulation velocity decreases and the holdup increases at a constant temperature of 298 K. In addition, it was found

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<tbody>
<tr>
<td>Voigt and Schugerl\textsuperscript{100}</td>
<td>air</td>
<td>$D_L = 0.20 \text{ m}$ $L = 3.81 \text{ m}$ perforated plates</td>
<td>$V_g = 0.012--0.078 \text{ m s}^{-1}$ $V_l = 8 \times 10^{-4}--4.4 \times 10^{-3} \text{ m s}^{-1}$ $\rho_l = 997--1006 \text{ kg m}^{-3}$ $\sigma = 0.049--0.073 \text{ N m}^{-1}$ $\mu_l = 0.88 \times 10^{-3}--1 \times 10^{-3} \text{ Pa s}$</td>
<td>Reduction in $d_v$ and $% FA$ increased $\varepsilon_0$</td>
</tr>
<tr>
<td>Pandit and Joshi\textsuperscript{78}</td>
<td>air (semibatch)</td>
<td>$D_L = 0.385$ $L = 1.35 \text{ m}$</td>
<td>$V_g = 0.03--0.25 \text{ m s}^{-1}$</td>
<td>The gas holdup increased in the presence of baffles</td>
</tr>
<tr>
<td>Kato et al.\textsuperscript{101}</td>
<td>air–water kerosene (cocurrent upflow)</td>
<td>$D_L = 0.066, 0.122 \text{ m}$ $L = 2, 2.2 \text{ m}$ perforated plates</td>
<td>$V_g = 0.015--0.13 \text{ m s}^{-1}$ $V_l = 0.001--0.01 \text{ m s}^{-1}$</td>
<td>$\varepsilon_0 = V_{cd}/30 + 3.3V_{cd}(0.8)$</td>
</tr>
<tr>
<td>Nishikawa et al.\textsuperscript{102}</td>
<td>air, N$_2$</td>
<td>$D_L = 0.10, 0.15 \text{ m}$ tap water</td>
<td>$V_g = 0.01--0.07 \text{ m s}^{-1}$ $V_l = 0.0--0.03 \text{ m s}^{-1}$</td>
<td>experimental data</td>
</tr>
<tr>
<td>Chen et al.\textsuperscript{103}</td>
<td>air–water (cocurrent upflow)</td>
<td>$D_L = 0.05, 0.075 \text{ m}$ $L = 3 \text{ m}$ 6 mesh SS wire screen</td>
<td>$V_g = 0.0--0.0822 \text{ m s}^{-1}$ $V_l = 0.0--0.0612 \text{ m s}^{-1}$ $d_v = 3, 5, 7.5, 8 \text{ mm}$</td>
<td>For Karr plates: $\varepsilon_0 = 0.0448V_g^{0.93}V_l^{-0.055}$</td>
</tr>
<tr>
<td>Chen and Yang\textsuperscript{104}</td>
<td>air</td>
<td>$D_L = 0.05, 0.075, 0.15 \text{ m}$</td>
<td>$V_g = 0--0.3 \text{ m s}^{-1}$</td>
<td>Homogeneous regime: $\varepsilon_0 = 2.4V_g^{0.4}d_g^{0.4}d_{pl}^{0.4} \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Vinaya\textsuperscript{105}</td>
<td>air</td>
<td>$D_L = 0.098, 0.154 \text{ m}$</td>
<td>$V_g = 0.0042--0.116 \text{ m s}^{-1}$</td>
<td>$H_C = 64%$</td>
</tr>
<tr>
<td>Yamada and Goto\textsuperscript{106}</td>
<td>hydrogen–water</td>
<td>$D_L = 0.02 \text{ m}$</td>
<td>$V_g = 0.01--0.13 \text{ m s}^{-1}$ $d_v = 0.2 \text{ mm}$</td>
<td>Homogeneous regime: $\varepsilon_0 = 0.59V_g^{0.3}d_g^{0.3} \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Dreher and Krishna\textsuperscript{108}</td>
<td>air–water (semibatch)</td>
<td>$D_L = 0.1, 0.15, 0.38 \text{ m}$</td>
<td>$V_g = 0.05--0.40 \text{ m s}^{-1}$ $L = 4, 6 \text{ m}$</td>
<td>$V_{aero} = 5.3 \times 10^{-2}--1.6 \times 10^{-3} \text{ m s}^{-1}$</td>
</tr>
<tr>
<td>Kemoun et al.\textsuperscript{109}</td>
<td>air–water (cocurrent)</td>
<td>$D_L = 0.2 \text{ m}$</td>
<td>$V_g = 0.016--0.167 \text{ m s}^{-1}$ $d_v = 6.35 \text{ mm}$</td>
<td>The role of gas pockets on $\varepsilon_0$ becomes negligible when column diameter exceeds 0.38 m</td>
</tr>
</tbody>
</table>

Table 5. Summary of Gas Holdup Studies in Sectionalized Bubble Column
that the value of \( V_S \) is higher \((C_1 = 0.319)\) and the fractional gas holdup \((0.174)\) is lower at a pressure of 0.1 MPa than the values of \( V_S \) \((0.285 \text{ and } 0.284)\) and fractional gas holdup at 0.5 MPa. In addition, the liquid circulation velocity was found to increase with an increase in temperature at a constant pressure.

The experimental values of axial-dispersion coefficient \((D_L)\) have been shown in Figure 10. It can be seen that, at all the values of \( V_G \), \( D_L \) increases with an increase in pressure. In order to understand this observation, CFD simulations of flow pattern were performed at both pressures \((0.1 \text{ and } 0.5 \text{ MPa})\) for the three systems and all the superficial velocities covered in the work. Figure 10 shows an excellent agreement between the experimental and predicted values of \( D_L \). It may be pointed out that, in all the cases, the values of average liquid circulation velocity \((V_C)\) and eddy diffusivity \((\nu_t)\) decrease with an increase in pressure. However, in spite of reduction in \( V_C \) and \( \nu_t \), the values of \( D_L \) increase in all the cases. Authors have made an attempt to understand the reasons for the observed increase in \( D_L \) with pressure in spite of the reduction in \( V_C \) and \( \nu_t \). For this purpose, a systematic analysis has been carried out on the parametric sensitivity of \( V_C \) and \( \nu_t \) on the axial-dispersion coefficient.

For instance, for the case of the \( \text{N}_2 \)-water system, ambient temperature and pressure at \( V_G = 0.104 \text{ m/s} \) and atmospheric pressure, the average liquid circulation velocity \((V_C)\) and eddy diffusivity \((\nu_t)\) were found to be 0.38 m/s and \(0.50 \times 10^{-3} \text{ m}^2/\text{s}\), respectively. The corresponding values at 0.5 MPa pressure were found to be 0.36 m/s and \(0.43 \times 10^{-3} \text{ m}^2/\text{s}\), respectively. For understanding the parametric sensitivity of \( V_C \) and \( \nu_t \) only one parameter was varied from their base values of 0.38 m/s and \(0.50 \times 10^{-3} \text{ m}^2/\text{s}\), respectively. The sensitivity of \( V_C \) is shown in Figure 11, and that of \( \nu_t \) is shown in Figure 12. From Figure 11, it can be seen that, at a constant \( \nu_t \), the value of \( D_L \) increases with an increase in \( V_C \). From Figure 12, it can be seen that the value of the axial-dispersion coefficient increases with a decrease in eddy diffusivity up to \(0.2 \times 10^{-3} \text{ m}^2/\text{s}\) (from \(0.5 \times 10^{-3} \text{ to } 0.2 \times 10^{-3} \text{ m}^2/\text{s}\) of the base case), and a further reduction in eddy diffusivity results in a decrease in the axial-dispersion coefficient.

The authors have made an attempt to understand the probable reasons behind the characteristic role of \( \nu_t \) on \( D_L \) as shown in Figure 12. When the eddy diffusivity is zero, the spreading of a tracer is practically zero (or very low because it occurs by
molecular diffusivity) at any intensity of bulk mean circulation. With only bulk convective motion, the added tracer keeps on circulating and the mixing time is very high or $D_L$ is very low. By incorporating some eddy diffusion, mixing time reduces (and $D_L$ increases). However, the mixing time attains a minimum at a $\nu_t$ value of $0.202 \times 10^{-3}$ m$^2$/s, and a further increase in $\nu_t$ results in an increase in $\theta_{\text{mix}}$.

When we talk of axial dispersion, it is the combined effect of $V_C$ and $\nu_t$ in the axial direction. Thus, we can imagine two extreme situations. At low values of $\nu_t$, the mixing is controlled by the bulk circulation, and a typical relationship is given by

$$\theta_{\text{mix}} \propto t_C$$

(20)

where $t_C$ is the circulation time given by

$$t_C = \frac{2H_D + D_C}{V_C}$$

(21)

For large $H_D/D_C$ ratio, eqs 20 and 21 simplify to

$$\theta_{\text{mix}} = \frac{bH_D}{V_C}$$

(22)

The other extreme occurs at high values of $\nu_t$, where the mixing is controlled by eddy diffusivity and the mixing time is given by

$$\theta_{\text{mix}} = \frac{cH_D^2}{\nu_t}$$

(23)

Thus, in the eddy-diffusivity-controlled regime, the denominator indicates reduction in mixing time with an increase in $\nu_t$. However, the $\theta_{\text{mix}}$ becomes proportional to $H_D^2$ as compared to the linear dependence in the circulation-controlled regime. Thus, in bubble columns where $H_D/D_C$ ratios are high, the conversion of dependence from $H_D$ to $H_D^2$ results in an increase in $\theta_{\text{mix}}$ with an increase in $\nu_t$. The above-mentioned qualitative description has been quantitatively explained by Lorenz et al.\textsuperscript{115}

The foregoing discussion provides an explanation for the effect of pressure on $D_L$. For instance, at a $V_G$ of 0.104 m/s, when the pressure is increased from 0.1 to 0.5 MPa, the values of $V_C$ and $\nu_t$ decrease by 3.78% and 14.59%, respectively. As a result, from Figures 11 and 12, it can be seen that the corresponding effect on $D_L$ is $-6.89\%$ and $+15.47\%$, respectively. The combined effect of $V_C$ and $\nu_t$ is a 16.63% increase in $D_L$ from 0.0086 to 0.0101 m$^2$/s, which compares favorably with the experimental value of 0.01 m$^2$/s. Similar exercises were performed for various gas–liquid systems, temperatures, and $V_G$, and the results are given in Figure 10. All these results quantitatively explain the reasons for the increase in $D_L$ with an increase in pressure.

A comparison between the experimental observations of Wilkinson et al.\textsuperscript{113} and the CFD predictions is shown in Figure 13. In all the cases, the value of $D_L$ was found to increase with an increase in pressure. Figure 13 shows an excellent agreement between the experimental observations and the CFD predictions.

For the CFD model developed by Lorenz et al.\textsuperscript{115} the experimental observations of Yang and Fan\textsuperscript{97} provide a critical test. In this set of experiments, the values of $D_L$ always decreased with an increase in pressure. The CFD predictions agree fairly well with the experimental observations of Yang and Fan\textsuperscript{97} (Figure 14) that the dispersion coefficient decreases with an increase in pressure.

The fundamental difference between the two sets of experiments (Wilkinson et al.\textsuperscript{113} and Lorenz et al.\textsuperscript{115}) and the results of Yang and Fan\textsuperscript{97} is that, for the corresponding gas–liquid systems under consideration, the gas holdup ($\varepsilon_{jG}$) increase with respect to pressure is different. In order to understand the parametric sensitivity of $\varepsilon_{jG}$, CFD simulations were performed under otherwise identical conditions of $V_G$, $D$, $H_D$, etc. The results are shown in Figure 15. It can be seen that an increase in $\varepsilon_{jG}$ initially results in a decrease in $D_L$ up to a certain critical

![Figure 11. Effect of variation of convection (with 100% eddy viscosity) on axial-dispersion coefficient (Lorenz et al.\textsuperscript{115}).](image1)

![Figure 12. Effect of variation of eddy viscosity (with 100% convection) on axial-dispersion coefficient (Lorenz et al.\textsuperscript{115}).](image2)

![Figure 13. Comparison between the simulations and the experimental data of Wilkinson et al.\textsuperscript{113} of axial-dispersion coefficient: (1) 0.1 MPa, (2) 0.5 MPa, and (3) 1 MPa (Lorenz et al.\textsuperscript{115}).](image3)
value of $\varepsilon_j$ and a minimum $D_L$. A further increase in $\varepsilon_j$ results in an increase in $D_L$. The important point is the actual $\varepsilon_j - V_C$ relationship that decides the nature of the holdup profile ($C_0$) and the bubble-rise velocity ($C_1$), which in turn decides the flow pattern ($V_C$ and $\nu_t$) and, hence, on $C_{ib}$, $C_1$, and the flow pattern. In order to confirm this reasoning, CFD simulations were carried out over a wide range of abovementioned parameters covered in the published literature. The results are shown in Figure 16, and the parity can be seen to be excellent.

6.1.4. Liquid-Phase Mixing and Axial Mixing in Sectionalized Bubble Column. In a bubble-column reactor, the agitating action of the rising gas bubbles generates interacting- or noninteracting-type multiple circulation cells. The inter-stage exchange velocity, $V_{ex}$, between the adjacent cells is responsible for the net transport of the liquid from one cell to another. The inclusion of baffle plates results in an isolation of these circulation cells, thereby reducing the exchange velocity and increasing the theoretical number of stages. Thus, the liquid-phase flow in the soaker approaches plug type. The exchange velocity or the effective liquid-phase Peclet number was found to be a function of superficial gas and liquid velocities, as well as percent free area and hole diameter of the sectionalizing plate. For a cascaded bubble column, Blass and Cornelius reported the following correlation to predict the effective number of stages:

$$N_{eff} = 1.061 \left( \frac{V_G FA}{V_{Lhole}} \right)^{-0.19}$$

The correlation is applicable over

$$1.3 < \left( \frac{V_G FA}{V_{Lhole}} \right) < 10 \text{ m}^{-1} \text{s}^{-1}$$

Palaskar et al. performed RTD studies on 0.062 and 0.2 m i.d. cold-flow sectionalized bubble columns, assuming it to be used for visbreaking application. The following conclusions can be drawn from their studies:

1. The extent of liquid-phase backmixing can be regulated using perforated plates.
2. The liquid-phase dispersion coefficient was found to be proportional to $V_L^{0.45 - 0.85}$ and $V_G^{0.12}$.
3. The introduction of gas phase by split mode of operation reduced the liquid-phase dispersion by 50–80% at lower liquid superficial velocities.
4. The liquid-phase dispersion in a large diameter column (0.2 m i.d.) was found to be 1.3–1.6 times higher than that in a small diameter column (0.062 m i.d.).

Further, the authors have correlated liquid-phase dispersion as a function of flow parameter as
\[
\ln \left( \frac{D_L}{V_L} \right) = \left( \frac{D_{CI}}{D_C} \right)^{-0.2} \left[ 0.023 \ln(FP)^2 + 0.2658 \ln(FP) \right] - 0.816 \tag{26a}
\]

where flow parameter FP is defined as follows:

\[
FP = \frac{(V_G)(\% \text{ Free Area})}{V_L} \tag{26b}
\]

The applicability of this correlation is largely limited by the regime of operation and lower values of gas and liquid superficial velocities. Dreher and Krishna\textsuperscript{106} carried out liquid-phase dispersion studies in three different sizes of bubble columns (0.1, 0.15, and 0.38 m i.d.) operated in semibatch mode.

The axial-dispersion coefficient was found to increase with increasing column diameter and superficial gas velocity. The exchange velocity, \( V_{ex} \), was found to increase with increasing percent free area of sieve plate and superficial gas velocity and found to be independent of column diameter. Recently, Kumar et al.\textsuperscript{81} performed radiotracer RTD studies on 0.1 m i.d. soaker visbreaker incorporated with and without perforated plates and operated at elevated pressure (1.2 MPa). The radiation count data were analyzed using two-parameter axial dispersion and tanks-in-series with backmixing type models. The study revealed that, in the presence of internals, the liquid-phase backmixing can be reduced by a factor of 3.

From the foregoing discussion, we summarize the liquid-phase axial mixing as follows. In a bubble column, the relationship between the liquid-phase dispersion coefficient (\( D_L \)) and the number of tanks-in-series is given by

\[
N_{ef} = Pe(0.5 + f) \tag{27a}
\]

where

\[
Pe = V_{L}H_D/D_L \tag{27b}
\]

and \( f \) is the ratio of backward flow to net flow. The value of \( f \) can be controlled by manipulating the design of sieve plates used for sectionalization. The value of \( f \) decreases with a decrease in free area, and in a limiting case of no weeping condition of the sieve plates, \( f \) becomes zero. Under this condition, the net liquid flow across the plate is managed by providing riser/downcomer depending upon the direction of net flow. For the intermediate case of finite weeping, eqs 24 and 26a can be used.

### 6.1.5. Weeping

The bubble coalescence occurring below the sieve trays is a statistical process during which the gas–liquid turbulent dispersion frequently reaches the plate and transfers the liquid to the next stage. In order to satisfy the continuity, the liquid from the upper section is also transferred to the lower section by the weeping mechanism. The undesired phenomena of weeping in a sectionalized bubble column can be explained on the basis of formation of a single bubble at the orifice, wherein the buoyancy and surface tension forces act upon the bubble. The bubble is detached from the orifice when buoyancy just exceeds the surface tension force. As a result, the upstream pressure reduces momentarily, and in order to counterbalance this pressure, the liquid above the plate starts weeping. Since the gas flow rate is continuous, the upstream pressure is immediately recovered and, thus, the weeping process continues over an entire cross section in a statistical manner. The formation of gas pockets are undesirable as they decrease gas–liquid interfacial area and reduce the effective reactor volume. Thus, the selection of sectionalizing plate hole diameter becomes an important criterion for designing sieve plates.

For a commercial-scale coal and residue hydrogenation process, Bakopoulos\textsuperscript{118} suggested the optimum range of hole diameter and free area to be 50–80 mm and 1–4%, respectively. Such a large hole diameter facilitates unidirectional flow of gas bubbles without gas-phase separation below the sieve plates for superficial velocities greater than 0.08 m s\(^{-1}\). Further, for successful experimental simulation of a high-pressure slurry bubble column, the author has recommended the fluid dynamic similarity between the following dimensionless groups for cold-flow and industrial process conditions,

\[
\frac{\rho_G}{\rho_{SL} V_{BM}}; \Omega_{SL} = \frac{g(\rho_{SL} - \rho_G)V_G(\Omega_{SL})^4}{\rho_G \sigma^3} \tag{28}
\]

where \( \Omega_{SL} \) is the modified Morton number.\textsuperscript{119}

The influence of solids concentration on macroscopic slurry viscosity is given as follows:

\[
\ln \Omega = 4.665 \ln \{ 5.7 \epsilon_S^{0.58} \sinh [ -0.71 \exp ( -5.8 \epsilon_S ) \ln ( \Omega/Mo )^0.22 ] + 1 \} \tag{29}
\]

For \( d_p < 10 \mu m \) or nonsettling slurries, the macroscopic viscosity is estimated as follows:

\[
\mu_{SL} = \mu_L \left( 1 + \frac{\rho_S + \rho_L}{\rho_L} \epsilon_S \right) \tag{30}
\]

### 6.1.6. Methodology for Predicting Reactor Performance

It may be pointed out that scarce information is available with regard to the adequate quantification of gas holdup and mixing time in industrial-scale visbreakers. In the absence of any design data, the preliminary estimation of gas holdup and liquid mixing time in industrial visbreakers can be performed by adopting the following methodology.

1. For a given capacity, the information related to the product yields can be made available from the respective refinery.
2. The assay data of each of the pseudo-boiling fractions (TBP curve, specific gravity, etc.) and their respective yields including the steam wt %, operating temperature, and pressure are given as an input to the equilibrium flash module in the ASPEN or similar simulation engine.
3. The flash calculations can be performed using property method such as Peng–Robinson or SRK equations of state (EOS), while for the prediction of transport properties, the respective methods have been reported by Filho and Sugaya.\textsuperscript{70}
4. From the obtained volumetric flow rates, the mean superficial gas and liquid velocities are calculated and correspondingly can be used in eqs 22–27 for calculation of average gas holdup in the soaker. In the case of coil, the average gas holdup can be estimated using the correlation of Hughmark.\textsuperscript{120} Thus, mean liquid-phase residence time or the effective volumes of the coil and the soaker can be evaluated.
5. The liquid-phase dispersion coefficient, \( D_L \), can be estimated using eqs 17 and 18 with \( V_{L_{bas}} = 0.09 \text{ m s}^{-1} \).\textsuperscript{84} From the knowledge of \( D_L \), the mixing time can be calculated as follows:

\[
\theta_{mix} = \frac{0.5 H_D^2}{D_L} \tag{31}
\]

The knowledge of mixing time gives us an idea of soaker behavior at respective operating conditions. If \( \theta_{mix} \ll \tau_{mean} \), then the soaker can be said to be fully backmixed and the fuel oil produced will be of inferior quality. Conversely, if \( \theta_{mix} > \tau_{mean} \), then the reaction is said to be partially completed, thereby reducing the overall conversions and selectivity toward the mid-
distillates. For an optimum performance, $\theta_{\text{mix}}$ should be comparable with $r_{\text{mean}}$, and this can be achieved using suitable internals.81

6.2. Mathematical Modeling. 6.2.1. Introduction. The coil and the soaker units of a visbreaker can be broadly classified as $G-L$ systems wherein the generated gas, vaporized low-boiling hydrocarbons, and superheated steam together act as a dispersed phase, while the visbroken residue acts as a continuous (liquid) phase. Thus, the former can be represented as a two-phase pipe-flow reactor, while the latter can be represented as a bubble-column reactor. It is well-known that the visbreaking reactions proceed via free radical mechanism and preferentially take place in the liquid phase. The extent of conversion occurring in the coil as well as in the soaker drum mainly depends on the process severity and the quality of the feedstock. The process temperature influences the cracking-reaction rate constants, whereas the feed flow rate decides the liquid-phase residence time in the coil and the soaker. The soaker-outlet pressure has an indirect effect on the liquid-phase residence time. Increasing the pressure suppresses the vaporization of low-boiling fractions, thus increasing the liquid-phase holdup and, consequently, the liquid-phase residence time ($\tau_L$). In industrial visbreakers, the superficial gas velocity ($V_G$) is typically 2–5 times that of the superficial liquid velocity ($V_L$), and this proportion may change with the extent of residue conversion, the operating pressure, and the quantity of steam injected in the coil. This leads to a relative slip condition between the liquid and vapor phases in the coil as well as in the soaker. Because of the associated slip, the thermodynamically calculated gas holdup significantly differs from the one calculated on the basis of the slip velocity ($V_s$). Thus, the regime of operation may change with the extent of the residue conversion, i.e., in the case of the coil, the regime may change from dispersed bubble to slug or annular type, while for the soaker, it may change from homogeneous to transition or heterogeneous type. Therefore, the model should take into account these effects so as to predict the liquid-phase residence time precisely.

The earlier studies on heavy oil processing included the seven-lump kinetic scheme for residue hydrotreating proposed by Mosby et al.121 in which each lump was an industrially important boiling fraction, viz. gas, naphtha, mid-distillates, gas oil, and hard-to-crack and easy-to-crack vacuum residues. For the evaluation of kinetic constants, the authors assumed that each hydrotreating unit behaved as a completely backmixed reactor. The model predictions were found to be in close agreement with the experimental yields. Further, a more detailed kinetic model for an industrial Dubb’s unit was proposed by Castellanos et al.66 In their approach, the feed and the product hydrocarbons were represented by a set of discrete pseudo-components, characterized by their true boiling point, API gravity, and molecular weight. The pseudo-components were categorized according to the number of carbon atoms present in these compounds. The coil was considered as a plug-flow reactor, and the end effects were neglected. The thermophysical properties, heat transfer coefficients, and feed and product enthalpies were also accounted for in the model. The activation energies and the frequency factors were correlated as a function of molecular weight of the reacting and product species. The model parameters were optimized using Powell’s method to match the industrial unit data. Though the model accurately predicted the reﬁnery yields, the complexity of the model restricted its application to the coil-visbreaking units only. In a more realistic approach for heavy oil hydroconversion in the slurry reactor, Carbonell and Guirardello122 combined the zero-order turbulence model with Mosby’s lumped-reaction scheme. The simulations were performed in two steps: in the first step, the hydrodynamics was established by calculating the pressure drop in the bed, the radial gas and slurry holdup distribution, the effective eddy viscosity, and the liquid-phase velocity proﬁle. In the second step, the thermal cracking reactions were superimposed by accounting the radial variations in these transport properties so as to predict the heavy oil conversion. Their study revealed that the liquid recirculatory patterns (backmixing) strongly affect the product yields. However, the validation of the experimental data was not performed using these models. In another approach, the coil-soaker was modeled as a plug-flow reactor (PFR) coupled with continuously stirred tank reactors (CSTRs) in series, and the rate constants were tuned to match the industrial visbreaker yields.123 The furnace pressure drop was estimated using the Beggs and Brill124 correlation. The model was able to predict the coil pressure drop, the coil-soaker temperature profiles, and the residue conversion within a narrow range of accuracy. However, the model was found to be feed-specific and accounted for only a single cracking reaction of VR to gas and gasoline.

Kulkarni125 extended a similar approach for modeling a pilot-scale coil-soaker visbreaker. The primary objective of this study was to eliminate the discrepancy between the pilot-plant yields and those predicted using the kinetic constants estimated from

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**Figure 17.** Five-lump, seven-rate parameter series—parallel kinetic model (Kataria et al.18).

**Figure 18.** Schematic representation of the coil and the soaker as PFR coupled with $j$ equal volumes of CSTRs in series superimposed with interstage backmixing.
the batch reactor data. This was achieved by multiplying the kinetic constants with appropriate scaling coefficients (α). The coil was considered as a dual plug-flow reactor, while the soaker was modeled as CSTRs in series with interstage backmixing. The model employed five-lump parallel kinetic scheme (Figure 17), the radiotracer RTD information gathered for the soaker equipped with/without internals, and the obtained pilot-plant visbreaking data. The α values were estimated by performing the least-squares analysis of the pilot-plant data and predicted product concentrations for each of the feeds. These modified rate constants can then be used for the estimation of industrial visbreaker product yields.

6.2.2. Mathematical Model Development. The coil and the soaker can be schematically represented as a PFR coupled with j equal volume CSTRs in series superimposed with interstage backmixing (Figure 18). The backmixing coefficient was defined as the fraction of the liquid-phase residue recycled back and is given as \( f = \frac{m_b}{m_i} \). The backmixing ratio was assumed to be constant for all the stages.

The preheater and the reaction coil were heated externally by immersing them in the molten salt bath maintained at the desired temperature. The batch reactor studies have shown that the cracking reactions initiate above 400 °C; hence, only the coils (no. 4, 5, 6) in the reaction zone were considered in the model development. To compensate for the heat losses from the surface as well as from the endothermic nature of the cracking reactions, heaters were provided on the outer surface of the soaker vessel, unlike industrial soakers, which are adiabatic reactors. The soaker inlet and outlet temperatures were controlled by changing the electrical power input delivered to these heaters. Since the information regarding the exact power delivered to the soaker was unknown, the heat added to the soaker was estimated from the inlet and outlet enthalpies (calculated on the basis of temperature differential across the soaker and the respective conversion) and the heat of reaction. The heat losses to the surroundings were compensated in the heat flux added to the soaker. Kulkarni has described the pertinent subject in detail.

The generalized correlation describing the variation in the liquid-phase volumetric flow rate is given as follows:

\[
Q_L = \left( \frac{m_i}{\rho_L} \right) \left( \alpha L + \psi \right) \exp(-\alpha y_{150}^\circ C) \tag{32}
\]

\[
Q_G = \left( \frac{m_i}{\rho_g} \right) \left( \beta L + \psi \right) \exp(-\alpha y_{150}^\circ C) \tag{33}
\]

The regressed values of the density–holdup correlation coefficients for the three feedstocks are listed in Table 6. The steady-state dimensionless material balance equation representing the material balance for each species can be written as

\[
\frac{d\psi_{VR}}{dz} = -\frac{\rho_L \varepsilon L A_c L}{m_i (y_{VR} + y_{VGO})} k_{123a} y_{VR} \tag{35}
\]

\[
\frac{d\psi_{VGO}}{dz} = \frac{\rho_L \varepsilon L A_c L}{m_i (y_{VR} + y_{VGO})} (k_{2} y_{VR} + k_{5} y_{VGO}) \tag{36}
\]

\[
\frac{d\psi_{LGO}}{dz} = \frac{\rho_L \varepsilon L A_c L}{m_i (y_{VR} + y_{VGO})} (k_{3} y_{VR} + k_{5} y_{VGO}) \tag{37}
\]

\[
\frac{d\psi_{Gas}}{dz} = \frac{\rho_L \varepsilon L A_c L}{m_i (y_{VR} + y_{VGO})} (k_{3} y_{VR} + k_{5} y_{VGO}) \tag{38}
\]

The energy balance equation to calculate the dimensionless temperature profile for the coil is given as follows:

\[
\frac{dy}{dz} = \frac{\rho_L \varepsilon L A_c L}{m_i (y_{VR} + y_{VGO})} (k_{1} y_{VR} + k_{2} y_{VGO}) \tag{39}
\]

The energy balance equation to calculate the dimensionless temperature profile for the coil is given as follows:

\[
\frac{d\psi}{dz} = \left( \frac{1}{\beta + \sum_{i=VR}^{G} C_{pi} \frac{dy}{dz}} \right) \tag{40}
\]

\[
\Delta H_R = [(k_1 + k_2) y_{VR}^* + (k_6 + k_7) y_{VGO}^*] \Delta H_R^* \tag{41}
\]

The heat of reaction of 800 kJ/kg for the products boiling below 204 °C was assumed. The liquid and vapor viscosities were averaged over the studied temperature range. The average specific heats were obtained from Kern and are listed in Table 7. The vapor- and liquid-phase viscosities were estimated using correlations proposed by Dean and Stiel and Twu. The liquid-phase thermal conductivity values were obtained from Mallan et al.

The reaction coil was divided into two zones, viz. fired section and unfired section. In the first zone, heat transfer occurs from molten salt bath to the coil to raise and maintain the temperature of the reaction mixture to a desired value. The bath temperature was assumed to be 20 °C higher than the coil-outlet temperature. The temperature rise in this zone was nonlinear and is given by eq 40. The second zone included a transfer line connecting the furnace outlet to the soaker. Because there was no additional heat input to this section, the temperature drop occurring along the coil length can be attributed to the endothermic nature of the reaction and the heat loss to the surroundings. Since the coil-outlet and soaker-inlet temperatures were known for this section, a uniform linear temperature gradient was assumed.

The initial conditions to solve eqs 35–41 are as follows:

At \( z = 0 \), \( y_{VR} = y_{VGO} \), \( y_{VGO} = y_{VGO} \), \( y_{LGO} = 0 \), \( y_{Gas} = 0 \), \( y_{Gas} = 0 \), \( \psi = 1.0 \).

The coil inside heat transfer coefficient was estimated using the procedure described below. For laminar flow, the following correlations are recommended to compute the heat transfer coefficient.

For \( Gz < 100 \),

\[
(Nu)_{lm} = 3.66 + \frac{0.085 Gz}{1 + 0.047 Gz^{2/3}} \left( \frac{\mu_w}{\mu_g} \right)^{0.14} \tag{43}
\]

For \( Gz > 100 \),

\[
(Nu)_{lm} = 1.086 Gz^{2/3} \left( \frac{\mu_w}{\mu_g} \right)^{0.14} \tag{44}
\]

For the case of turbulent and transition regime (\( NRe > 2100 \))

\[
Nu = 0.0116 (Re_M^{2/3} - 125) Pr^{1/3} \left( 1 + \left( \frac{d_1}{D_1} \right)^{2/3} \right) \tag{45}
\]

The above equations are for a straight tube and are applicable
for a helical coil with the substitution of $D_g/D_c$ for $L/D$ terms in the Graetz number. Thus, the Graetz number is written as:

$$G_z = Re_M Pr_M \left( \frac{d_c}{D_h} \right)^{0.5} \quad (46)$$

The soaker was considered as an axially dispersed reactor and modeled using a series of equal volume tanks with interstage backmixing. Each section was considered as a CSTR, and the exchange mass flow rate ($m_e$) was assumed to be constant. The information about the number of theoretical stages ($N$) and the backmixing coefficient ($f$) for a soaker incorporated with or without internals can be obtained from the actual plant RTD studies or from the published literature discussed in Section 6.1.3. For species VR and VGO, the model was represented by tanks-in-series with backmixing, while for LGO, Ga, and $G$ fractions, it turns out to be a simple CSTR-in-series type model; because they are in the vapor phase, the vapor-phase backmixing was found to be insignificant. The liquid-phase holdup in each tank was determined by the drift flux model used in the reported values of $C_1$, $V_{bas}$, and $m$. The material and energy balance equations for various species are given as follows.

For the first tank,

$$y_{VR0} - (1 + f)(y_{VR} - r_{VR})|_1 + \frac{f y_{VR}}{y_{VR} + y_{VGO}} = 0 \quad (47)$$

$$y_{VGO0} - (1 + f)(y_{VGO} - r_{VGO})|_1 + \frac{f y_{VGO}}{y_{VR} + y_{VGO}} = 0 \quad (48)$$

$$y_{LGO0} - (1 + f)(y_{LGO} - r_{LGO})|_1 = 0 \quad (49)$$

$$y_{Ga0} - (1 + f)(y_{Ga} - r_{Ga})|_1 = 0 \quad (50)$$

$$y_{Ga0} - (1 + f)(y_{Ga} - r_{Ga})|_1 = 0 \quad (51)$$

$$y_{LGOj} = y_{VGO0} - (1 + f)(y_{VGO} - r_{VGO})|_j + \frac{f y_{VGO}}{y_{VR} + y_{VGO}} = 0 \quad (52)$$

For the $j$th tank, where $2 \leq j < (N - 1)$,

$$y_{VRj} - (1 + f)(y_{VR} - r_{VR})|_{j-1} + \frac{f y_{VR}}{y_{VR} + y_{VGO}} = 0 \quad (53)$$

$$y_{VGOj} - (1 + f)(y_{VGO} - r_{VGO})|_{j-1} + \frac{f y_{VGO}}{y_{VR} + y_{VGO}} = 0 \quad (54)$$

$$y_{LGOj} - y_{LGOj-1} + r_{LGOj-1} = 0 \quad (55)$$

$$y_{Ga} - y_{Ga} + r_{Ga} = 0 \quad (56)$$

$$y_{LGOj-1} - y_{LGOj-1} + r_{LGOj-1} = 0 \quad (57)$$

$$y_{Ga} - y_{Ga} + r_{Ga} = 0 \quad (56)$$

$$y_{Ga} - y_{Ga} + r_{Ga} = 0 \quad (57)$$

The reaction rate expressions are given as follows:

$$r_{VR} = -\frac{H_c \varepsilon_k IC_1 D_{VR}}{V_L} \quad (65)$$

$$r_{VGO} = -\frac{H_c \varepsilon_k IC_1 D_{VGO}}{V_L} - \frac{k_{sG0} y_{VR}}{V_L} \quad (66)$$

$$r_{LGO} = -\frac{H_c \varepsilon_k IC_1 D_{LGO}}{V_L} - \frac{k_{sG0} y_{VGO}}{V_L} \quad (67)$$

$$r_{Ga} = -\frac{H_c \varepsilon_k IC_1 D_{Ga}}{V_L} - \frac{k_{sG0} y_{Ga}}{V_L} \quad (68)$$

$$r_{Ga} = -\frac{H_c \varepsilon_k IC_1 D_{Ga}}{V_L} - \frac{k_{sG0} y_{Ga}}{V_L} \quad (69)$$

$$\Delta H_j = -\frac{q' \pi D_c H_c}{m_e T_0} + \frac{\Delta H^*}{m_e T_0} (r_{Ga} + r_{Ga}) \quad (70)$$

The average gas holdup in each tank can be obtained using the drift flux model of Zuber and Findlay $^{131}$ as follows:

$$\frac{V_G}{\varepsilon_G} = C_0 (V_G + V_L) + V_{bas} (1 - \varepsilon_G)^m \quad (71)$$

$$\varepsilon_G = 1 - \varepsilon_G \quad (72)$$

where $C_0 = 1.0$, $V_{bas} = 0.1$, and $m = 1.75$.
to be $2.81$. This high value of the backmixing coefficient suggests that the soaker behavior is closer to that of a backmixed reactor, and thus, $\alpha$ values were estimated assuming a case of a single CSTR. The best test for any kinetic model is the prediction of experiments that were not used for the parameter estimation. Hence, using these $\alpha$ values, the yields were predicted for the case of a soaker incorporated with internals, and the equivalent number of tanks representing the observed yields was found out.

6.2.3. Algorithm for Parameter Estimation.

(1) The number of tanks ($N$), feed mass flow rate ($m_f$), coil-inlet temperature ($T_{in}$), coil-outlet temperature ($T_{out}$), soaker-inlet temperature ($T_{in,s}$), residue and product concentrations ($x_i$), and dimensionless soaker-outlet temperature ($\Psi$) were read as an input data file in the main program. Also, the other data input included geometrical details of the coil and the soaker, specific heats, coil-inlet concentrations, and activation energy and frequency factors (Tables 7 and 8).

(2) The appropriate guess values of scaling coefficients were provided to initialize the calculation procedure in the main program.

(3) Equations 35–40 were integrated numerically using the fourth-order Runge–Kutta method with the step size equal to 0.001.

(4) The estimated coil-outlet concentrations and the temperature were fed as an input to the soaker. Also, these values along with the experimental conversion (150 $^\circ$C) and the soaker-outlet temperature provided the heat flux ($q'_f$) from the heating elements to the soaker. The heat energy added per stage was assumed to be constant.

(5) The product concentration data for each experimental run served itself as an initial guess for starting the iterations.

(6) The algebraic equations 53–64 were iteratively solved in the backward direction, i.e., from $j=N$ to $j=2$. Care has been taken to avoid non-negative values of the variables, and the material balance was checked during each calculation over each tank. Similarly, for each iteration, the converged values of liquid-phase holdup were obtained using the Newton–Raphson method.

(7) The convergence criteria defined by eqs 47–52 was checked. If the absolute value of $f(x)$ defined by eqs 47–52 were less than 0.0001, then the solutions were said to be converged.

(8) If the conditions defined in step 6 were not satisfied, then the new input values of concentration and temperature were obtained using the Newton–Raphson method.

(9) Steps 5–7 were repeated until the converged profiles of concentration and temperature were obtained.

(10) The evaluated product concentrations and the dimensionless soaker-outlet temperature were compared with the pilot-plant data.

(11) Steps 3–10 are repeated for each experimental run, and the sum of squares of errors function (SSE) defined by the following equation was minimized using the modified steepest-descent method so as to obtain the optimum values of the scaling coefficients.

$$SSE = \sum_{j=1}^{\text{tot}} \sum_{i=\text{VR}}^{\text{VR}} \left( \frac{y_{\text{exp}}^{(i)}}{y_{\text{exp}}^{(i)}} - \frac{y_{\text{pred}}^{(i)}}{y_{\text{pred}}^{(i)}} \right)^2$$

Table 8. Arrhenius Parameters, $E/R$ (K) and $A$ (s$^{-1}$) Used for Model Simulation

<table>
<thead>
<tr>
<th>Pathway</th>
<th>BHVR, AMVR</th>
<th>VB Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>BX $\rightarrow$ G</td>
<td>$1.54 \times 10^{23}$</td>
<td>$38.98$</td>
</tr>
<tr>
<td>BX $\rightarrow$ Ga</td>
<td>$2.51 \times 10^{23}$</td>
<td>$37.94$</td>
</tr>
<tr>
<td>BX $\rightarrow$ LGO</td>
<td>$6.25 \times 10^{23}$</td>
<td>$30.91$</td>
</tr>
<tr>
<td>VG $\rightarrow$ BX</td>
<td>$8.52 \times 10^{23}$</td>
<td>$51.24$</td>
</tr>
<tr>
<td>VG $\rightarrow$ LGO</td>
<td>$6.67 \times 10^{23}$</td>
<td>$44.68$</td>
</tr>
<tr>
<td>VG $\rightarrow$ Ga</td>
<td>$1.68 \times 10^{28}$</td>
<td>$53.20$</td>
</tr>
<tr>
<td>VG $\rightarrow$ G</td>
<td>$1.29 \times 10^{40}$</td>
<td>$55.53$</td>
</tr>
</tbody>
</table>

7. Conclusions and Suggestions for Future Work

The overall conclusions and the suggestions for future work may be summarized as follows:

(1) The trend of processing heavy crudes in the refineries has brought about a renewed interest in bottom-of-the-barrel upgradation. Visbreaking, because of its low capital cost, low operational upsets, and ease in handling residue of any quality, is one of the important residue upgradation processes and contributes about 33% of the total residue processing capacity. Visbreaking provides low-cost conversion, especially when idle equipment can be modified for visbreaking service. Furthermore, visbreaking projects can be implemented rapidly and a quick payout can be expected.

(2) The physicochemical properties of the products of visbreaking, extent of variation in the gas and distillate yield, coking propensity, and crackability, are highly dependent on the physicochemical properties of the feedstocks.

(3) The study pertaining to the characteristic property of a large number of feeds shows that (i) H/C ratio increases with increasing API gravity, (ii) sulfur and nitrogen contents decrease...
primary reactions involve Cali splitting and C ar
n-C7 asphaltenes and CCR
n-C7 asphaltenes and CCR
n-C7 asphaltenes and CCR
carbons. The
and interclass conversions, a comprehensive mechanism involv-
and saturates content.
content while being inversely proportional to the asphaltenes
contents decrease with increasing API gravity of the feed.
by making the use of parallel and parallel

(5) On the basis of the reported observation in distillates yield and interclass conversions, a comprehensive mechanism involving primary and secondary reactions has been proposed. The primary reactions involve C al-C al splitting and C C-C al dearomatization to give distillates formation, while secondary reactions (via H-abstraction, cyclization, condensation, and aromatization) give interclass conversions that follow the order: sature > aromatics > resins > asphaltenes.

(6) There exists a threshold concentration beyond which asphaltenes precipitate out of the malten phase as a second phase (also known as mesophase). In the mesophase, asphaltenes undergo a high rate of condensation, aromatization, and dealkylation to give coke.

(7) Fouling phenomena is the chronic effect of secondary reactions, viz. polymerization and condensation. Fouling limits the maximum achievable skin temperature and on-stream time and increases the pressure drop.

(8) The kinetics reported is based on the pseudo-components (based on the solubility, boiling-point cuts, and carbon number) by making the use of parallel and parallel—consecutive models. The parallel model explains only the thermal cracking of the feed to distillates and does not consider further cracking of the already-cracked products. However, parallel—consecutive models consider the cracking of the products and the secondary reactions paths as well and, thus, explain the coke formation. The activation energy of cracking and coke-formation reactions can range from 22 to 83 kcal/mol. The large variation in these values is mainly due to variation in the feed characteristics and different lumping approaches (different combinations of compounds) used.

(9) Lumped kinetic models are often used to describe visbreaking reactions. The reaction rate parameters such as activation energy and frequency factor determined on the basis of large boiling range or SARA analysis alone fail to reflect the effect of feed properties. Thus, the detailed hybrid models using narrow boiling range or carbon number are highly desirable over which thermodynamic properties such as critical temperature or pressure, mean molecular weight, accentric factor, and solubility parameter do not vary appreciably. Though such models will be too complex, they are expected to determine the close dependency between the two. The rate constants so estimated can then be used for accurate prediction of commercial visbreaker yields.

(10) Single-coil, two-coil, coiler-soaker-type, and sectionalized-soaker visbreaking processes have shown increasing degree of performance in terms of conversion and selectivity.

(11) Of late, there is an increasing trend of getting more of distillates out of visbreaking in addition to conventional benefits in terms of viscosity and pour-point reduction of the residual feedstocks. Shell International Oil Products has developed the Shell Deep thermal conversion (SDTC) process, which runs at much higher severity levels. Distillates are maximized by incorporating Shell Visbreaking Vacuum Flashing. 21

(12) The production of liquid fuels and chemicals out of synthesis gas is making rapid strides because of the ever-diminishing crude oil reserves. The gasification of visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas is making rapid strides because of the ever-diminishing crude oil reserves. The gasification of visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbroken residue to synthesis gas has been a promising route. About 18% of the total gasification capacity worldwide rests with visbreaking residu...
processes use high hydrogen pressure and catalytic additives such as molybdenum and are intended to operate at severe conditions. The reaction chemistry and fluid properties in these hydroconversion processes are fundamentally different from the conventional visbreaking regime.

(14) The soaker may operate in transition or heterogeneous regime depending upon the feed type and operating conditions. The comprehensive gas holdup and bubble-size distribution measurements over a wide range of physicochemical properties and gas–liquid superficial velocities under moderate-to-high pressure need to be performed. The data so obtained can be used to estimate the transition velocity ($V_{trans}$) and can be subsequently incorporated in the correlations to predict gas and liquid holdups for an unknown G–L system.

(15) The diagnostic tools such as noninvasive gamma ray tomography and radiotracer residence time distribution studies can be fruitful in throwing light on the hydrodynamics of the reactor. These techniques have been successfully tested and standardized on laboratory cold-flow and pilot-plant units. The information gathered from the above studies can be used in assessing the performance of existing coil-soaker visbreaker units and incorporated in the powerful CFD codes to predict internally consistent velocity, eddy viscosity, and gas holdup profiles.

(16) In the black-box approach, the output yields are regressed as a function of input variables such as temperature, LHSV, feed density, asphaltenes, and CCR content using best-fit correlations. The approach of preliminary models (in which coil-soaker is assumed as a plug-flow reactor coupled with n-CSTRs in series or a one-dimensional axially dispersed reactor) includes iterative solution of the equations of continuity, momentum, and energy to predict axial pressure, temperature, and product profiles. The axial pressure drop is calculated using friction factor defined on pseudo-phase properties (single-phase flow), while the model parameters (apparent activation energy and frequency factor) are tuned to match the plant data. However, these methods may give erroneous results when tested for an unknown feed and operational variables outside the range covered. The detailed two- and three-dimensional process models that take into account the kinetics and equilibrium flash calculations still need to be developed.

(17) Soaker internals are designed on the basis of the hydrodynamic data obtained on cold-flow laboratory setup or pilot-scale units in terms of liquid-phase mixing time, residence-time distribution, differential pressure drop, radial gas-holdup profiles, and product yields. Such experiments are often time-consuming and require a considerable capital expenditure. This can be avoided by using the commercial CFD software packages. The hydrodynamic parameters such as velocity, holdup, pressure, and eddy viscosity can be estimated for different set of internals using Euler–Euler type models. The profiles so obtained can be used very well to predict the RTD or mixing time for a given percent free area, hole diameter, and pitch of the baffle plate.

(18) Hydrovisbreaking and aquaconversion being multiphase reactions, the mass transfer and chemical reactions are of significant importance. The possible sequence of steps through which these reactions occur can be given as (i) mass transfer of steam/H$_2$ to catalyst surface, (ii) reforming reaction (in the case of aquaconversion) to produce molecular hydrogen, (iii) adsorption of hydrogen on the catalyst surface, (iv) diffusion of hydrocarbon species on the catalyst surface, (v) hydrogenation reactions (radical saturation) on the catalyst surface, and (vi) desorption of hydrogenated species into the bulk. It is desirable to study the effect of temperature, H$_2$/steam partial pressure, type of catalyst and its loading, particle size (for supported catalyst), and speed of agitation on product yields to understand the reaction mechanism and determine the rate-controlling step. Further, the compatibility of additives (sulfur, oil-miscible metal compounds) with the feed properties needs to be explored.

Acknowledgment

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Nomenclature

- $A$: frequency factor (s$^{-1}$)
- $a_1$, $a_2$, $a_3$: regression coefficients in eq 32
- $A_c$: cross-sectional area (m$^2$)
- AMVR: Arabian mix vacuum residue
- $A_p$: surface area (m$^2$)
- AR: atmospheric residue (wt %)
- $Ar$: aromatics (wt %)
- $A_s$: asphaltenes (n-heptane insolubles) (wt %)
- $B$: constant
- $b$: constant used in eq 22
- $b_1$, $b_2$, $b_3$: regression coefficients in eq 33
- BDE: bond dissociation energy (kcal mol$^{-1}$)
- BHVR: Bombay high vacuum residue
- $c$: constant used in eq 23
- $C$: concentration
- $C_{al}^*$: aliphatic carbon
- $C_a$: aromatic carbon
- $C_d$, $C_i$: drift flux constant
- $c_1$, $c_2$, $c_3$: regression coefficients in eq 34
- CCR: Conradson carbon residue (wt %)
- $C_p$: average specific heat (kJ kg$^{-1}$ K$^{-1}$)
- $C_{p,Feed}$: feed average specific heat (kJ kg$^{-1}$ K$^{-1}$)
- $C_{p,steam}$: steam average specific heat (kJ kg$^{-1}$ K$^{-1}$)
- $d_b$: bubble diameter (m)
- $d_{max}$: maximum stable bubble diameter (m)
- $d_c$: coil diameter (m)
- $D_c$: column diameter (m)
- $D_{ref}$: reference column diameter (m)
- $D_{helix}$: helix diameter (m)
- $D_i$: liquid-phase axial dispersion coefficient (m$^2$ s$^{-1}$)
- $d_{hole}$: hole diameter (m)
- $dQ'$: differential heat input (W)
- $d_z$: incremental coil length (m)
- $E$: activation energy (kcal mol$^{-1}$)
- $f$: backmixing coefficient
- $FA$: free area
- FP: flow parameter
- $Fr$: Froude number
- $g$: acceleration due to gravity (m s$^{-2}$)
- $G$: gas fraction (C$_1$–C$_4$) (wt %)
- $Ga$: gasoline (C$_5$–150 °C) (wt %)
- $Ga_n$: initial concentration of gasoline at zero residence time (wt %)
- $G_m$: mass velocity (kg m$^{-2}$ s$^{-1}$)
- $G_i$: initial concentration of gas component at zero residence time (wt %)
- $G_{gra}$: Graetz number
$h$ = film thickness (m)  
$H/C$ = molar hydrogen-to-carbon ratio (mol mol$^{-1}$)  
$H_c$ = cell height (m)  
$H_{CL}$ = clear liquid height (m)  
$H_D$ = dispersion height (m)  
$j$ = tank number  
$k$ = first-order reaction rate constant (s$^{-1}$)  
$k_{fH}, k_f$ = first-order rate constants of the n-C$_7$ soluble and asphaltene, respectively (s$^{-1}$)  
$k_i, k_i'$ = first-order reaction rate constant for $i$th species (s$^{-1}$)  
$k_{1-7}$ = rate constants (s$^{-1}$)  
$k_{1234}$ = $k_1 + k_2 + k_3 + k_4$ (s$^{-1}$)  
$k_{567}$ = $k_5 + k_6 + k_7$ (s$^{-1}$)  
$L$ = column or coil length (m)  
LGO = light gas oil (150–350 °C) (wt %)  
LGO$_o$ = initial concentration of LGO at zero residence time (wt %)  
m = holdup profile index  
m' = mass flow rate (kg s$^{-1}$)  
m$_b$ = liquid backmixed flow rate (kg s$^{-1}$)  
m$_f$ = feed mass flow rate (kg s$^{-1}$)  
m$_k$ = steam mass flow rate (kg s$^{-1}$)  
MMTPA = million metric tons per annum  
$M_o$ = Morton number  
$M_{OSL}$ = slurry Morton number  
$M_W$ = molecular weight (kg kmol$^{-1}$)  
$N$ = actual number of CSTRs  
n = number of holes  
n' = scale-up index  
NA = naphthenic aromatics (wt %)  
n-C$_3$ = n-pentane insolubles (wt %)  
n-C$_7$ = n-heptane insolubles (wt %)  
dnat = number of data points  
$N_{eff}$ = effective number of CSTRs  
$N_u$ = Nusselt number  
PA = polar aromatics (wt %)  
$Pe$ = Peclet number  
$Pr$ = Prandtl number  
$Pr_m$ = two-phase Prandtl number  
$q$ = backward flow rate (m$^3$ s$^{-1}$)  
$q'$ = heat flux (W m$^{-2}$)  
$Q$ = net volumetric flowrate (m$^3$ s$^{-1}$)  
$Q_l$ = total flow rate given as $(Q + q)$, (m$^3$ s$^{-1}$)  
$Q_{li}$ = liquid-phase volumetric flowrate (m$^3$ s$^{-1}$)  
$Q_{L}$ = vapor-phase volumetric flow rate (m$^3$ s$^{-1}$)  
$R$ = gas constant (cal gmol$^{-1}$ K$^{-1}$)  
$R'$ = column radius (m)  
$R_d$ = radius of disk (m)  
$Re$ = Reynolds number  
$Re_m$ = two-phase Reynolds number  
$Rs$ = resins (wt %)  
$r$ = radial distance (m)  
r$_i$ = rate of reaction for the $i$th species (mol s$^{-1}$)  
r$_0$ = reaction rate for gas (mol s$^{-1}$)  
r$_{GAO}$ = reaction rate for gasoline (mol s$^{-1}$)  
r$_{LGO}$ = reaction rate for LGO (mol s$^{-1}$)  
r$_{VRGO}$ = reaction rate for VGO (mol s$^{-1}$)  
r$_{VR}$ = reaction rate for VR (mol s$^{-1}$)  
$S$ = sulfur (wt %)  
$S_A$ = saturates (wt %)  
SARA = saturates, aromatics, resins, and asphaltenes  
SF = stability factor  
SI = severity index (s$^{-1}$)  
SSE = sum of square of errors  
SX = stability index  
$T$ = reaction temperature (K)  
t = reaction time (s)  
$T_0$ = coil inlet temperature (K)  
$T_b$ = bath temperature (K)  
$T_c$ = circulation time (s)  
$T_I$ = toluene insoluble (coking) (wt %)  
$T_S$ = soaker outlet temperature (K)  
$U_i$ = overall inside heat transfer coefficient (W m$^{-2}$ K$^{-1}$)  
$V$ = tank volume (m$^3$)  
$V_{br}$ = terminal bubble rise velocity (m s$^{-1}$)  
$V_{BM}$ = rise velocity of maximum stable bubble (m s$^{-1}$)  
$V_c$ = liquid circulation velocity (m s$^{-1}$)  
$V_{cx}$ = interstage exchange velocity (m s$^{-1}$)  
$V_S$ = superficial gas velocity (m s$^{-1}$)  
VGO = vacuum gas oil (350–500 °C) (wt %)  
VGO$_o$ = initial concentration of VGO at zero residence time (wt %)  
$V_L$ = superficial liquid velocity (m s$^{-1}$)  
$V_{i(0)}$ = liquid centerline velocity (m s$^{-1}$)  
$V_{h, hole}$ = liquid-phase hole velocity (m s$^{-1}$)  
$VR$ = vacuum residue (wt %)  
$VR_o$ = initial concentration of VR at zero residence time (wt %)  
$V_s$ = slip velocity (m s$^{-1}$)  
$V_{SL}$ = superficial slurry velocity (m s$^{-1}$)  
$V_{mall}$ = unhindered rise velocity of small bubbles (m s$^{-1}$)  
$V_{trans}$ = transition velocity (m s$^{-1}$)  
$x_{GO}$ = fractional conversion to gas–gasoline fraction (<236)  
$y_i$ = concentration of $i$th species  
$y_{GAO}$ = dimensionless concentration for gasoline on wt basis  
$y_{LGO}$ = dimensionless concentration for LGO on wt basis  
$y_{VR}$ = dimensionless concentration for VR on wt basis  
$y_{VR}$ = dimensionless concentration for VR on wt basis  
$y_{N}$ = concentration at soaker outlet for $i$th species  
$y_{N}$ = concentration at soaker outlet for $i$th species  
$y_{N}$ = concentration at soaker outlet for $i$th species  
$z$ = reactor length  
Greek Letters  
$\bar{e}$ = fractional average holdup  
$e_G$ = fractional gas holdup  
$\bar{e}_G$ = average fractional gas holdup  
$e_L$ = fractional liquid holdup  
$\bar{e}_L$ = average fractional liquid holdup  
$e_S$ = fractional solid holdup  
$\bar{e}_{trans}$ = regime transition gas holdup  
$\Delta \rho_G$ = radial density gradient  
$\mu_L$ = liquid viscosity (Pa s)  
$\alpha$ = scaling coefficient  
$\beta$ = constant  
$\Delta H$ = enthalpy change (kJ kg$^{-1}$)  
$\Delta H_R$ = heat of reaction calculated on basis of liquid feed conversion (kJ kg$^{-1}$)  
$\Delta H^*$ = heat of reaction (kJ kg$^{-1}$)  
$\Delta H_{L}$ = specific heat of reaction for products boiling below 204 °C (kJ kg$^{-1}$)  
$\phi$ = surface drag (m s$^{-1}$)  
$\Omega$ = slurry correction factor  
$\sigma$ = surface tension (N m$^{-1}$)  
$\psi$ = temperature  
$v_i$ = eddy diffusivity (m$^2$ s$^{-1}$)  
$\mu$ = viscosity (Pa s)  
$v_L$ = kinematic viscosity (m$^2$ s$^{-1}$)
\( r_l \) = liquid-phase residence time (s)
\( r_{mean} \) = mean residence time (s)
\( \theta_{mix} \) = mixing time (s)
\( \mu_s \) = slurry viscosity (Pa·s)
\( \rho \) = density (kg m\(^{-3}\))
\( \rho_g \) = gas density (kg m\(^{-3}\))
\( \rho_{atm} \) = gas density at atmospheric pressure (kg m\(^{-3}\))
\( \rho_l \) = liquid density (kg m\(^{-3}\))
\( \rho_0 \) = standard density at 15 °C (kg m\(^{-3}\))
\( \rho_s \) = slurry density (kg m\(^{-3}\))

Subscripts
\( am \) = arithmetic mean
\( b \) = bulk
\( G, L \) = gas, liquid
\( i \) = species G, Ga, LGO, VGO, VR
\( j \) = run number
\( lm \) = logarithmic mean
\( M \) = mean
\( ndat \) = number of data points
\( w \) = wall

Literature Cited
