Visbreaking studies on Aghajari long residue

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Visbreaking studies on Aghajari long residue (370°C+) have been conducted in a continuous bench-scale unit at different severity conditions. The effects of temperature and residence time on the yields and properties of the visbroken distillates and residues have been studied. The kinetics of cracking has been determined to be first order.

(Keywords: kinetics; cracking; visbreaking)

The high viscosity and pour point of petroleum residues render them unsuitable as fuel in industrial furnaces and refineries. Further, the increased domestic demands of middle distillates and light fuel oils provide economic incentives to upgrade petroleum residues. Residue upgrading is generally done through catalytic as well as thermal cracking processes, depending upon the nature of feeds and types and qualities of the desired end products. Visbreaking is a relatively inexpensive and versatile residue upgrading thermal process employed in the petroleum industry, primarily aimed at lowering the viscosity of petroleum residues. In addition, this process provides better feeds for catalytic processing[1] by reducing the molecular size, thus facilitating the ready diffusion of feed molecules into the micropores of the catalysts employed, a primary condition for excellent catalytic results.

Recently, Le Page and Davidson[2] have reviewed the different families of conversion processes for petroleum residues and heavy oils, and concluded that the conversion of high-molecular weight species proceeds through a free-radical mechanism. Singh[3] has compared two modes of operations in visbreaking, namely coil and soaker cracking, on the basis of economics and product qualities. Only limited data on the visbreaking of petroleum residues under different operating conditions and the effects of operating parameters on product yields and properties are available in the literature[4-6]. Recently, Tominaga *et al.*[7] have reported the visbreaking reactions of atmospheric residues from a number of crudes at three temperatures in the presence of diluents, e.g. nitrogen, hydrogen and tetralin, and discussed the effect of temperature on distillate yields and properties of visbroken residues. In subsequent papers[8-10] they have reported the structural analyses of feeds and visbroken residues employing ^{1}H-n.m.r., v.p.o. and g.p.c. techniques and have formulated reaction schemes or visbreaking pathways for different feeds.

As a part of the programme to develop correlations between the feed properties and product yields during visbreaking, as well as the effects of visbreaking severities on yield, qualities and structural changes of these products, investigations on the long residue (370°C+) of Aghajari crude in a laboratory-scale continuous-flow coil reactor under different severity conditions were undertaken and the data obtained are reported in this paper. Kinetic parameters and severities of operations are computed using temperature, feed flow rate and wt% yield of undesired 150°C$^-$ fraction as conversion. Attempts have also been made to explain the variation of wt% yields and properties of various visbroken distillates and residues with severities in terms of chemical composition of feed, which can be used to understand the cracking behaviour of residues under different process conditions.

EXPERIMENTAL

A continuous-flow bench-scale set-up (see *Figure 1*) wherein the feed is heated to cracking temperature in a preheater stainless steel coil (6 mm i.d. and 2.1 m length) and fed continuously to another stainless-steel reactor coil (6 mm i.d. and 1.6 m length) maintained at the required temperature by a molten salt bath, has been used in this study; two flash chambers are added for separating gaseous and liquid products. Feed flow rates and temperature profiles were measured by pulse-feeder pump and a number of sheathed iron/constantan thermocouples respectively. Experiments were carried out at temperatures from 427 to 500°C, total pressure of 17 bar (1700 kPa) and feed flow rates varying from 2.04 to 2.90 l/h. The repeatability of yield data has been found to be ±0.3 wt% for gases and ±0.5 wt% for liquid products.

The liquid visbroken products obtained in each experiment were batch fractionated into IBP–150, 150–250, 250–370 and 370–500°C cuts. These fractions, together with 150°C+, 370°C+ and 500°C+ residues, were examined for their major physicochemical characteristics by ASTM/IP standard methods.

RESULTS AND DISCUSSION

The physicochemical characteristics, together with its ASTM distillation (D-1160) data, of Aghajari long residue (370°C+), obtained from atmospheric distillation unit of a refinery, are reported in *Table 1*. The viscosity of the feed is 352 cSt at 50°C, which is very high compared with that specified for the LV grade fuel oil (80 cSt at 50°C). The data of *Table 1* reveal that the residue is of intermediate nature (K_{UOP} = 11.6), with a relatively high sulphur content (2.15 wt%).

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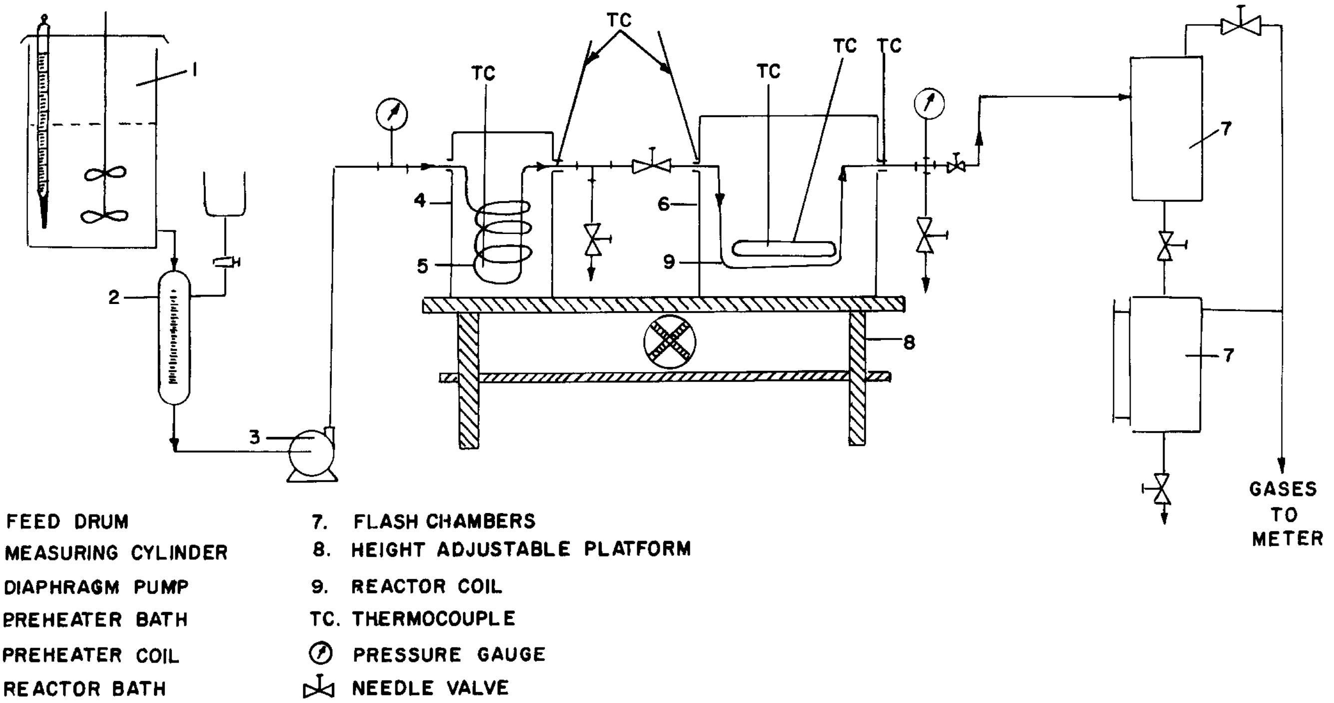

Figure 1 Process flow diagram of the unit

Table 1 Feedstock characteristics of Aghajari atmospheric residue

Characteristics	Values
Density, d_4^{15}	0.9565
°API	16.5
Kinematic viscosity (cSt) at 50°C	352.0
at 98.9°C	30.0
Flash point, °C	192+
nC_5 insolubles, wt%	5.66
Molecular weight	550
Pour point, °C	30
Carbon residue, wt% (Conradson)	7.9
Nitrogen content, wt%	0.355
Ash content, wt%	0.024
Sulphur content, wt%	2.15
K_{UOP}	11.6
ASTM distillation D-1160 (Corrected to ASTM pressure 760 mmHg)	
IBP, °C	242
5% vol, °C	341
10% vol, °C	368
20% vol, °C	414
30% vol, °C	442
40% vol, °C	468
50% vol, °C	501
60% vol, °C	513

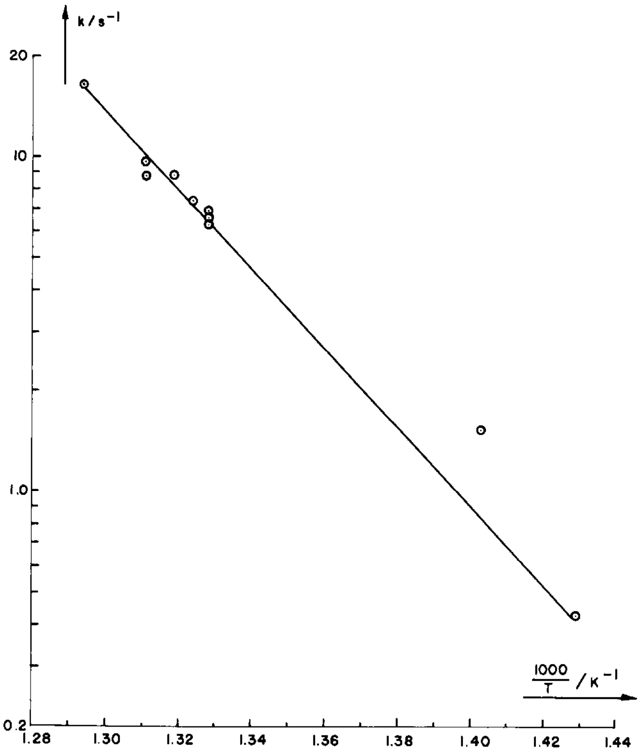

Figure 2 Arrhenius plot

The visbreaking severity is defined as a parameter taking into account the two operating variables—the cracking temperature and the residence time (based on inlet liquid flow). Other parameters such as pressure affect residence time indirectly. Thus, considering the unimolecularity of liquid phase visbreaking, the rate of cracking can be expressed as

$$\frac{dx}{d\tau}=k(1-x) \tag{1}$$

where $k=k_0\,e^{-E/RT}$ (2)

In the present study, the term $(\tau e^{-E/RT})$ containing residence time and cracking temperature has been used to quantify severity. From the Arrhenius plot of *Figure 2*, which suggests the nature of cracking reactions to be first order, the activation energy has been calculated to be 224.8 kJ/mol. The pre-exponential factor calculated from the slope of the graph of $ln(1-x)$ vs. severity (*Figure 3*) is found to be $2.17\times10^{12}\,s^{-1}$, which also supports the first-order nature of the cracking reactions at the operating conditions used in the present study.

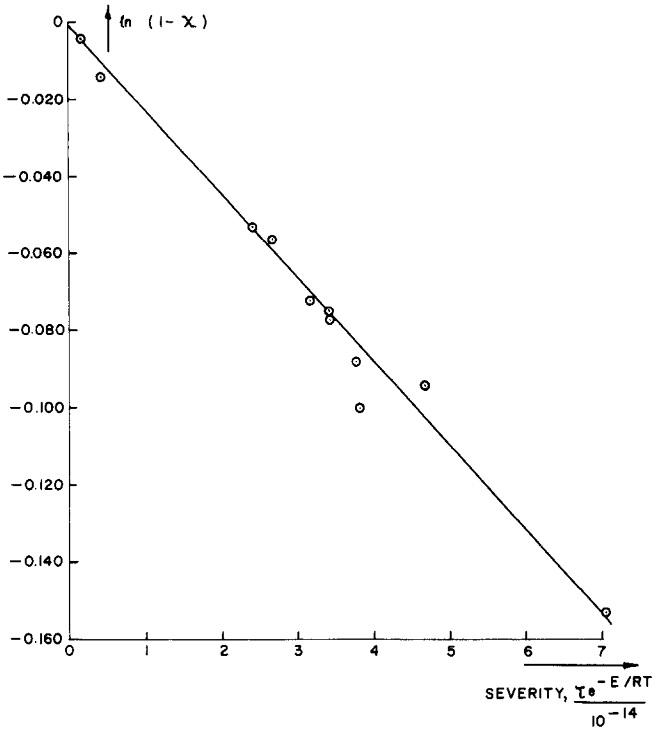

Figure 3 Graph between ln $(1-x)$ versus severity

Gases and distillates

The variations in yield of gaseous and distillate products with increasing conversion (wt % yield of 150°C$^-$) are shown in *Figure 4*. It is evident from this Figure that yields of gases and the IBP–150°C cut increase very systematically with the conversion. However, the yield of the kerosine fraction (150–250°C) shows a relatively sharp increase after about the 7 wt % conversion level. The reason for this behaviour may be that after this conversion other higher distillates, i.e. gas oil and vacuum gas oil, also start cracking. This is also corroborated by variations in the yield of gas oil (250–370°C) and vacuum gas oil (370–500°C) with conversion. The increase in gas oil yield beyond 7 wt % conversion is relatively slower, but the yield of vacuum gas oil shows a slightly decreasing trend with an increase in conversion. This may be attributed to the lower activation energy of relatively larger molecules in this boiling range compared with lighter distillates, thus increasing cracking with increase of severity[3].

Some of the important physicochemical properties of distillate fractions have also been determined. The Reid vapour pressure of naphtha fractions (IBP–150°C) has been found to be within 0.26±0.09 bar (26±9 kPa). The olefin content, as determined by the FIA method, has been found to vary between 25–50 vol % and 20–40 vol % in the naphtha and kerosine fractions, respectively. The distribution of sulphur has been found to occur within 0.58±0.02 wt %, 0.66±0.06 wt % and 1.63±0.24 wt % in the naphtha, kerosine and gas oil fractions, respectively. These values are high, because of the high sulphur content of the feed itself (2.15 wt %) and the lowest bond energy of C–S bonds[2] (272 kJ/mol) compared with other bonds. The smoke point of kerosine fractions, 19±1 mm, and the diesel index of gas oils (250–370°C), 42±2, do not vary significantly with severity. These values are slightly inferior to the values specified by ISI (SP = 18 mm and DI = 45) for these fuels.

Residues

The yield patterns of various visbroken residues with increasing conversion level are presented in *Figure 5*. Whereas the yield of the 150°C+ residue shows a regular decreasing trend with increased conversion, the 370°C+ residue shows a relatively slower decrease in yield with increased conversion beyond the 7 wt % conversion level. A similar trend has been observed in the yield pattern of the 500°C+ residue. Such behaviour may be attributable to the cracking of most of the higher-molecular-weight compounds and/or cleavage of most of the alkyl substituents on condensed aromatic clusters up to this conversion level, due to lower activation energy, and beyond this the cracking rate may reduce due to remaining lower-molecular-weight compounds having higher activation energy and/or due to the formation of refractory aromatic clusters.

A few important physicochemical properties of 150°C+ and 370°C+ residues have also been estimated, to judge their quality. The most significant property is the variation of viscosity at 50°C with conversion, compared with feed. The viscosity reductions, i.e. ratio of the viscosity of visbroken products (residue) at 50°C to that of feed at 50°C, for 150°C+ and 370°C+ residues, have been plotted with increasing conversion and are shown in *Figure 6*. The viscosity reduction curve for the 150°C+ residue reveals that up to a conversion level of 7 wt %, the

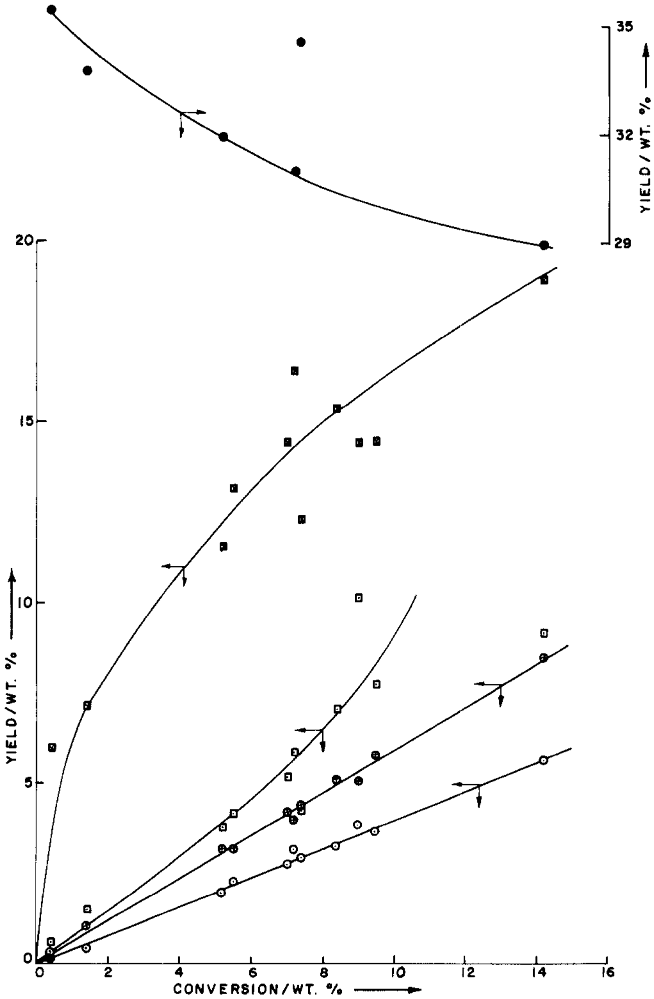

Figure 4 Weight % yields of distillates versus conversion; ○, gases; ⊗, IBP–150°C; □, 150–250°C; ⊠, 250–370°C; ●, 370–500°C

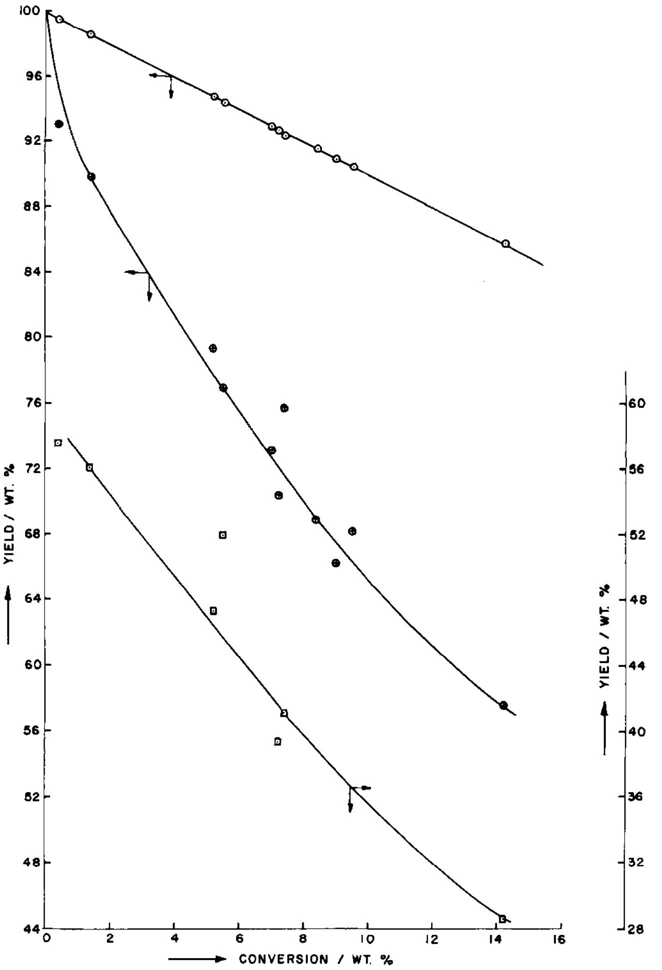

Figure 5 Weight % yields of residues versus conversion; ○, 150°C+; ⊗, 370°C+; □, 500°C+

decrease in viscosity is steeper; beyond this level the decrease is relatively slower. This behaviour may be attributed to the relatively higher contribution of polymerization/condensation of visbroken products after this conversion level and/or the relatively slower cracking rate of the remaining compounds of higher activation energy, as explained earlier. *Figure 6* reveals that the viscosity of 370°C+ visbroken residue is higher than the feed at all conversion levels studied and this increase in viscosity is nearly constant up to a conversion level of 7 wt% and then increases more rapidly with increased conversion. The reason for this behaviour is that during the initial stages (low conversions), the distillate formation due to cleavage of side alkyl chains and cracking of larger molecules produces hydrogen-deficient condensed and/or unsaturated structures, as higher hydrogen levels in distillates are derived from the feed itself, and thus the viscosity is higher due to condensation and polymerization. After the 7 wt% conversion level, these secondary reactions become significant compared with cracking and, hence, increase the viscosity steeply with conversion. This inference can also be corroborated from *Figure 6*, showing the variation of Conradson carbon residue values of 370°C+ residue with conversion, which also shows a relatively higher increase in CCR value after a nearly 7 wt% conversion level.

Pour points of 150°C+ and 370°C+ residues are found to vary from −21 to +18°C and +9 to +27°C respectively, which are low compared with the feed (+30°C). The CCR values are found to vary within 8.5–11.9 wt% for the 150°C+ and 9.1–19.2 wt% for the 370°C+ residue. The $n\mathrm{C}_5$-asphaltene data for respective residues are 6.7–10.0 wt% and 5.7–11.8 wt% higher than that of the feed data (5.66 wt%). Sulphur content has been found to be 2.50±0.45 wt% and 2.57±0.42 wt% in 150°C+ and 370°C+ residues respectively. The flash point of 150°C+ residue is reduced (occurring between 90 and 102°C) while that of the 370°C+ residue is slightly higher (230°C) compared with that of the feed (192°C). Thus, 150°C+ residues, obtained at the severity conditions studied, meet the ISI specifications of LV grade fuel oil as regards the kinematic viscosity at 50°C (<80 cSt) and sulphur content (<3.5 wt%), but do not meet the flash point specification (>66°C). The viscosity and flash point data of the 370°C+ residue do not meet the specifications of even HV grade fuel oil. Thus, these residues need proper cutter stocks for blending to meet the specifications as HV grade fuel oil.

CONCLUSIONS

The kinetics of visbreaking of Aghajari long residue (370°C+) under varying severity conditions show that the primary reactions are of a first-order nature, with an activation energy of 225 kJ/mol. A sharp deviation observed in the wt% yield, as well as the properties of distillates and residues at about the 7% conversion level, reveals that beyond this conversion the secondary reactions become significant. The physicochemical

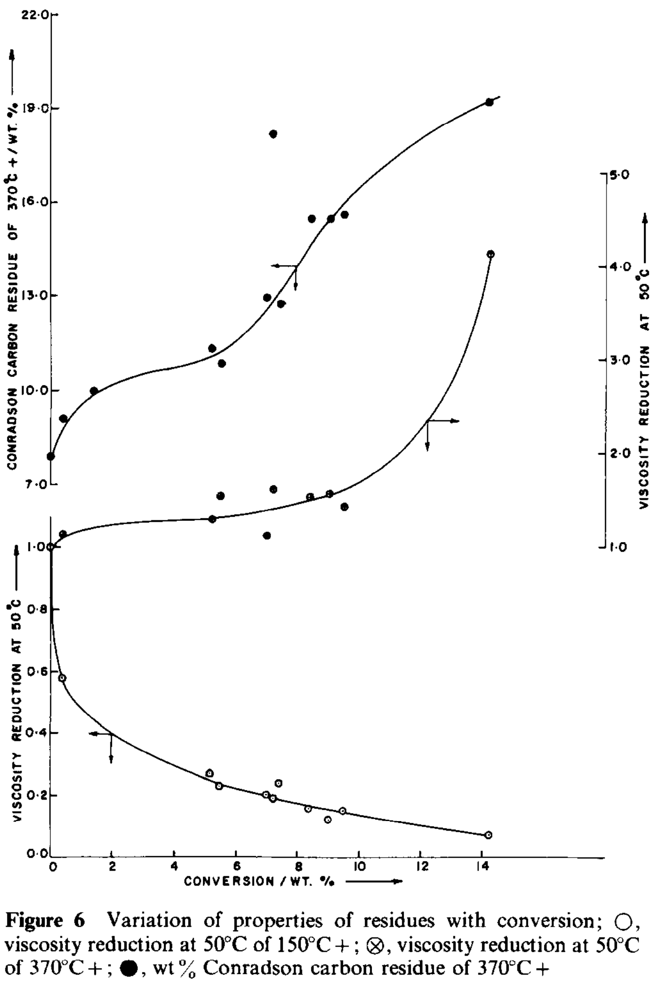

Figure 6 Variation of properties of residues with conversion; ○, viscosity reduction at 50°C of 150°C+; ⊗, viscosity reduction at 50°C of 370°C+; ●, wt% Conradson carbon residue of 370°C+

properties of visbroken middle distillates are slightly inferior to the ISI specifications, but the light fuel oils (150°C+) obtained meet the LV grade fuel oil specifications at all severity conditions studied.

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NOMENCLATURE

E	Activation energy (kJ/mol)
k	Specific rate constant (s^{-1})
k_0	Pre-exponential factor (s^{-1})
R	Gas constant (8.3143×10^{-3} kJ/mol, K)
T	Cracking temperature (K)
x	Weight fraction of product boiling below 150°C
τ	Residence time based on liquid feed entering the coil (s)