SYNOPSIS

Among many sophisticated separation techniques of practical interest in petroleum and petrochemical industries, adductive crystallization is gradually gaining importance in recent years. In general, this consists of entrapping a particular component from a mixture of hydrocarbons within a crystalline solid phase constituted by a specific material added to the system. Urea is one among these adductive agents and is capable of crystallizing out into a complex with n-paraffins, as well as with many other straight chain-type compounds. Hence urea adduction technique has made it possible to separate n-paraffins from a mixture of n- and iso-praffins and thus offers a process to attain very low pour points for lubricating and transformer oils and also to obtain high quality jet fuels, special dry-cleaning solvents, etc. But as many of process details are not available in published literature and also, since the kinetic aspects of the problem have not yet been studied to a fuller extent, the present investigation on urea adduction is undertaken with the following objects in view :

i) to study the effect of process variables on adduct formation with a) aqueous urea solution and b) solid urea

ii) to deduce a suitable kinetic mechanism for complex formation with solid urea

iii) to apply liquid-fluidization technique in urea dewaxing.

A chapter-wise abstract of the thesis is presented below.

Chapter 1 Introduction and Literature Survey.

Chapter 2 Preliminary Investigations

i) Characteristics of reactants and various solvents used

a) Wax source : Pressable wax distillate of boiling range, 280-435°C, obtained from crude oil of Nahorkatiya, Assam (India), is used. Its pour point is 42.0°C, resin content 4.2% by weight and adductable wax content 39.33% by weight.

b) Urea : Prills of urea having shape factor 0.92 to 0.95 are used. Its purity is found to be 98.5% by weight. Urea particles of different sizes ranging from -7+8 to -16+22 B.S.S. mesh are employed in various experiments.

c) Methanol is used as an activator. Benzene, Toluene and Naphtha (100-125°C) are the three solvents chosen for adduct decomposing purpose in experiments on urea-dewaxing in fluidized bed reactor.

ii) Determination of stoichiometric ratio (urea/wax) in the adduct

It is experimentally found that the stoichiometric ratio (urea/wax) in the adduct increases slightly in proportion with the amount of wax reacted as can be noted from the results given below :

Parts of wax reacted per 100 parts by weight of the same present initially	Stoichiometric ratio (Urea/Wax) by weight
8.04	3.166
20.10	3.167
40.15	3.171
60.15	3.176

Chapter 3 Adduct Formation with Aqueous Urea Solution

i) Effect of operating variables on induction period

a) Induction period sharply decreases, to start with, and then gradually with the increasing stirrer speed.

b) For a definite amount of urea in aqueous phase in excess of its saturation value corresponding to reaction temperature, induction period for adduct formation becomes minimum.

c) Induction period decreases linearly with the increase in initial urea to wax ratio taken in the reactant-mixture. On the other hand, it shows an increasing trend with the decrease in wax concentration in liquid phase.

d) By seeding, induction period can be reduced considerably, but not completely. Also, finer the seed material less is its requirement for a desired depression in induction period.

e) Induction period is reduced to about one-third of its value noted in the absence of activator at very small activator (methanol) concentrations of the order of 0.015 part by weight per part of oil phase.

ii) Effect of operating variables on equilibrium wax-yields

a) For the same urea to water ratios taken, wax-yields are found to be proportional to the amount of urea added into the reaction-mixture.

b) Concentration of urea in aqueous phase (which is in equilibrium with adduct formed) increases linearly with reaction temperature.

iii) Aggregate properties of complex

Granularity of adduct is found to be very much dependent upon the operating variables. Granules of about 2 mm size are obtained at a reaction temperature of 35°C, for the values of urea to water and urea to oil ratios of 2 and 0.5 respectively.

Chapter 4 Adduct Formation with Solid Urea in Batch Reactor

i) General aspects

a) The rate of adduct formation increases initially in proportion with activator (methanol) concentration reaching a maximum corresponding to its maximum miscibility in the liquid reactant-system. With further increase in activator concentration, the rate decreases gradually.

b) Wax-yield for a given reaction time first increases with dilution of oil and after attaining a maximum value, it decreases with further dilution.

c) Urea-conversion for a given reaction time increases sharply with the decrease in particle size of urea. On the other hand, it decreases with the decreasing wax to urea ratio taken initially in the reactant-system.

ii) Kinetic aspects

Nucleation rate mechanism comprising of branching and overlapping of nuclei agrees with the experimental data both in acceleratory and decay periods upto the urea-conversion of the order of 90% by weight. Activation energy in the decay period of adduct formation is found to be equal to 2.55 kcals per gram mole.

iii) General correlation on rate data

For methanol concentrations greater than about 0.012 part by weight per part of liquid phase, the fractional conversion of urea by weight (x) is related to reaction time in minutes (θ) by

$$x / (1-x) = (3.289)\, 10^{-3}\, (100\,\theta)^{k'_n}$$

The exponent k'_n is obtained with the knowledge of various operating variables by

$$k'_n = 8.888\, X_{po} \cdot X_m^{0.1124} \cdot (W_{po}/W_{uo})^{0.0593} \cdot \left[R_o (1-\epsilon_{pu}) \right]^{-0.2525}$$
$$e^{-51.88 X_r} \cdot e^{4.165(T-308)/T}$$

This correlation agrees with the major part of the experimental data within an accuracy of about ± 4%.

Chapter 5 Urea Dewaxing in Fluidized Bed Reactor

A. Adduct Formation Step

i) General aspects

a) During adduct formation chances of aggregation are found to be very high with urea particles of size less than -12+14 B.S.S. mesh.

b) For the same activator concentration, the particle porosity of adduct obtained in fluidized bed experiments is found to be less than that observed in batch experiments.

ii) Kinetic aspects

Fluidized bed reactor data conforms with the nucleation rate mechanism of the type branching and overlapping of nuclei, as has been observed in batch experiments.

B. Adduct Decomposition Step

i) General aspects

Adduct decomposition rates are found to be very much dependent upon the type of solvent used and decomposing temperature, but are not influenced by the change in adduct particle size and porosity.

ii) Kinetic aspects

The rate data agree with the continuous-reaction model for adduct decomposition-reaction. Activation energy is found to be equal to 32.6 kcals/gm.mole and heat of decomposition, 49.4 kcals/gm.mole. The values remain the same irrespective of the type of solvents used (aromatics and non-aromatics), but the rate of decomposition varies depending upon their 'solvent-effect' on activity of wax in solution.

iii) Applicability on industrial scale

The following advantages are found to be feasible by employing fluidization technique in urea-dewaxing :

a) Minimum transportation of solids
b) No need of filtration-equipment
c) Possibility of continuous operation.