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NEW AND IMPROVED DISPERSION AND RECOVERY TECHNIQUES
FOR SLURRY PHASE CATALYSIS

Quarterly Report for the Period January—March 1984

By

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Work Performed Under Contract No. AC22-83PC60044

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New and Improved Dispersion and Recovery Techniques
For Slurry Phase Catalysis

Quarterly Report for the Period:
January - March, 1984

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Summary

A mathematical model has been developed for predicting the effects of various parameters such as recycle rate, permanent and temporary deactivation rate constants on catalyst activity. The intent of this analysis is to evaluate the importance of the ease at which a catalyst can be regenerated and to identify important catalyst properties associated with regeneration. A reactor (hydrotreater)-regenerator system having equal catalyst inventory in each unit is used as a basis for modeling. A fixed amount of fresh catalyst supply and spent catalyst withdrawal are assumed to be applicable to the reactor. The analysis showed that a small percent increase in the permanent deactivation rate constant relative to total deactivation rate constant has decreased the mean activity of the catalyst in the reactor significantly. In most cases, mean activity of the catalyst increased with increasing recycle rate. Whereas, the effect of regeneration rate constant on the catalyst activity was not significant compared to that of permanent deactivation rate constant.

Objective and Scope

Objective:

- To assess the effect of catalyst porosity, pore size distribution, and diffusion path length on coal liquefaction selectivity using different supported catalysts and to determine the relative importance of thermal and catalytic reactions on product selectivity.
- To study the effects of crystallite dispersion, catalyst porosities, pore size distributions and diffusional characteristics on overall activity.
- To identify catalyst deactivation/regeneration properties and to determine their effect on overall activity during coal liquefaction reactions.
- To characterize and evaluate the microsupported catalysts after coal liquefaction reactions in order to determine dominant mechanisms such as coking, sintering, or metals deposition encountered during coal liquefaction. This data will assist in the selection and tailoring of the most effective microsupported catalysts.
- To identify appropriate metal sulfides, supports and catalyst structures for slurry phase coal liquefaction and to integrate and optimize these characteristics so as to tailor and produce effective new slurry phase catalysts.

Scope:

The purpose of the present work is to study the relative effects of deactivation and regeneration on catalyst activity using a theoretical analysis. The temporary and permanent deactivation, the sum of which determines the total deactivation, would be studied as functions of catalyst properties. One way of achieving the above objective is to analyse a reactor (hydrotreater)-regenerator system in which a certain amount of deactivated

catalyst is continuously withdrawn, regenerated, and fed back to the reactor. The mean activity of the catalyst in the reactor can be used as a measure for studying the effects of deactivation and regeneration kinetics and catalyst properties.

Program Task Outline

Task 2.1. Catalyst Preparation

Task 2.2. Catalyst Characterization

Task 2.3. Catalyst Evaluation Using Coal

Task 2.4. Spent Catalyst Evaluation

Task 2.5. Catalyst Improvement

Acknowledgement

The work reported here was made possible by the efforts of the following personnel of the Auburn Coal Conversion Laboratory. Their contributions to this report and to the progress of this work are hereby gratefully acknowledged.

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Introduction

Various catalyst activity retardation phenomena severely limit the effectiveness of expensive supported transition metal catalysts in the catalytic upgrading of coal liquids. This catalyst activity retardation is caused by coking, metal deposition, and changes in catalyst properties in the reactor; however, a considerable amount of catalyst activity can be regenerated by oxidation of deposited coke or, possibly, some form of washing. The purpose of the present work is to study the relative effects of deactivation and regeneration on catalyst activity using a theoretical analysis, at least for the present time.. The temporary and permanent deactivation, the sum of which determines the total deactivation, would be studied as functions of catalyst properties. One way of achieving the above objective is to analyse a reactor (hydrotreater)-regenerator system in which a certain amount of deactivated catalyst is continuously withdrawn, regenerated, and fed back to the reactor. The mean activity of the catalyst in the reactor can be used as a measure for studying the effects of deactivation and regeneration kinetics and catalyst properties.

Background

Over the past few decades several processes have been developed to produce clean solid and liquid fuels from coal. Hydrotreatment involving catalytic hydrogenation and hydrocracking of the heavy coal liquids using a hydrogen rich gas is generally utilized to upgrade coal liquids. The activity of the catalyst used in the hydrotreating step diminishes with time and hence, the product quality as measured, for example by the degree of asphaltene conversion to oil, or heteroatom removal deteriorates. The degradation of the catalyst can be attributed to the deposition of carbonaceous material and heavy metals on the catalyst. As the rate of deactivation controls the

overall activity of the catalyst, if rapid deactivation takes place, it would be economical to regenerate the spent catalyst for maintaining a constant and high activity level in the hydrotreater. The purpose of the present work is to study the effect of catalyst regeneration and recycling on catalyst activity level in the reactor. In the following the deactivation and regeneration mechanisms are discussed. Also, a mathematical model has been developed for predicting the effects of various parameters such as recycle rate, permanent and temporary deactivation rate constants on catalyst activity. The intent of this analysis is to evaluate the importance of the ease at which a catalyst can be regenerated and to identify important catalyst properties associated with regeneration.

Catalyst Deactivation. Deactivation of a hydrotreating catalyst in coal liquids, which is a very complex phenomenon, may occur due to fouling, poisoning, sintering and loss of sulfur from the catalyst. Also, pore-plugging reduces the intra-particle diffusion of the reactants into the catalyst pores and hence reduces the rate of reaction. As observed by Sie (1980), the dominant deactivation mechanism depends upon the catalyst age. Sie observed three distinct stages of deactivation. An initial rapid decline in activity, a gradual intermediate decline followed by a rapid decline in the catalyst activity. The initial decline in activity was attributed to carbonaceous deposition on the catalyst with the overall effect of reducing the active catalyst sites by pore-plugging of the catalyst. Wolf and Afani (1982) reviewed the literature on catalyst deactivation due to coking. They noted that coke deposition is a complex multi-step reaction sequence involving adsorption, dehydrogenation, condensation, polymerization and cyclization of hydrogen deficit fractions. Hydrogen presence plays a key role in decreasing the rate of coke formation. Theoretically, all hydrocarbons present in the

feed material have the ability to produce coke deposits; the rates of these reactions differ according to their chemical structure, molecular weight and reaction conditions (Beuther, 1964). The reduction in catalyst activity due to carbon deposition is limited. For example, Plank and Nace (1955) observed that after the rapid initial loss in activity of the catalyst, the catalyst reached a semi-steady state activity level whereas the carbon deposition increased further with time.

The gradual intermediate decline in catalyst activity has been attributed to deposition of metals on the catalyst. These metals form a chemical bond with some of the atoms present in the catalyst and become an integral part of the catalyst. Consequently, metal deposition leads to a permanent type of deactivation which can only be removed to a limited extent by selective solvent reactions. Whereas, the carbonaceous deposits can be easily removed by oxidation and hence, coking can be considered a temporary type of deactivation. The effect of metals on catalyst activity can be selective. For example, accumulation of these metals reduces the hydrogenation activity. If the catalyst is regenerated by coke oxidation, some metals deposited are also dislocated and some activity is recovered by removal of these metals. However, the amount of regeneration by dislocation of metals is negligible compared to the amount of regeneration by coke removal.

Coke and metal deposition greatly reduce the free metal surface area and pore volume. Stiegal et al. (1982 a, b) have examined the effects of catalyst diameter and properties on the rate of deactivation in processing of coal slurries. The catalysts used were Amocat 1A catalyst, HDS-1442A and 1442B, all of which were Co-Mo/Al₂O₃ catalysts. The catalysts suffered a large reduction in surface area, pore volume, and average pore diameter due to coking and

metal deposition. Also as studied by Ocampo et al. (1978), most catalysts exhibit comparable activity after 18 hrs of operation irrespective of their initial activity. In other words, the metal type and composition of the catalyst had no significant effect on the final semi-steady state activity of the used catalyst. As deactivation mainly occurs due to coke deposition, regeneration can prove to be helpful to maintain a high activity level for a catalyst with a high initial activity.

The activity of a catalyst is measured by its productivity which is defined as the amount of product produced per unit time per unit weight of catalyst. Due to catalyst deactivation, the productivity of the catalyst decreases with time. One way of maintaining the product quality which can be defined as the concentration of a desired component in the product stream is to increase the reactor temperature. With an increase in the reactor temperature, the reaction rate increases, thus increasing the production rate of the desired component. However, in coal liquefaction, the reactor temperature can be increased only to a limited extent due to operational difficulties. The desired product quality can be maintained at a lower temperature by regenerating and recycling a fraction of the reactor hold-up. Thus, the catalyst deactivation rate can be maintained at a minimum level.

Catalyst Regeneration

As mentioned earlier, temporary deactivation occurs due to the deposition of carbonaceous material on the catalyst, and permanent deactivation occurs due to the deposition of metals and permanent changes in pore constrictivities. The loss of catalyst activity due to temporary deactivation can be restored by simple oxidation of the coke deposits. Several investigators have studied the regeneration characteristics of coal

liquefaction catalysts. Cable et al. (1981) determined the activity of Co-Mo/Al₂O₃ in its fresh, aged and aged-regenerated states. The aged catalyst contained approximately 20 wt% coke and 5 wt% metal contaminants. Coke was evenly distributed throughout the catalyst, whereas the metals were concentrated near the exterior of the catalyst. Regeneration in air at 450°C only partially restored the catalyst's original hydrodesulfurization activity but almost completely restored the hydrogenation and cracking activities. Stiegel et al. (1983) found that unimodal catalysts are capable of being restored to their original state upon regeneration, while bimodal catalysts suffer a small loss of surface area and pore volume upon regeneration. By regenerating the HDS Co-Mo/Al₂O₃ bimodal catalysts, the initial activity for coal conversion and product selectivity was restored.

Nalitham et al. (1984) studied the kinetics of coke oxidation for aged Ni-Mo/Al₂O₃ catalysts obtained from LC-Fining, PDU runs. Coke on the aged catalyst was primarily composed of carbon (11 wt%) though it also contained small amounts of hydrogen (0.6-0.7 wt%), nitrogen (0.3-0.4 wt%) and sulfur. The LC-Fining pilot unit consisted of two expanded-bed catalytic reactors. The catalyst aging history i.e., whether the catalyst was obtained from 1st or 2nd reactor, affects the regenerated catalyst properties. For example, 60% of the original activity as determined by the percent naphthalene hydrogenation was restored for the catalyst obtained from the first reactor; whereas 90% of the fresh catalyst activity was regenerated for the catalyst obtained from the second reactor. This difference was attributed to differences in the reactor liquid properties. The regeneration rate constant increased with oxygen partial pressure and oxidation temperature. Thus, from the above work it is seen that up to 50-90% of the original catalyst activity can be restored by regeneration.

Sensitivity of Hydrotreater Catalyst Activity to Regeneration Parameters.

As discussed earlier a fraction of the original activity of the catalyst can be restored by regeneration. The activity of the catalyst is primarily a function of the length of its residence in the reactor. The longer the catalyst stays in the reactor the more it deactivates because the deposition of carbon and metal on the catalyst increases with time. Each time the catalyst passes through the reactor some permanent deactivation takes place and when the catalyst is regenerated the original activity can not be restored even if the residence time in the regenerator approaches infinite.

Petersen (1960) and Rudd (1962) studied the deactivation and regeneration of the catalyst. Petersen proposed a mathematical method to calculate the steady state activity of a catalyst bed with a fixed mass being recycled (after regeneration). The method is based on a residence time distribution function. The activity of the catalyst particle is a function of its initial properties, its history within the reactor-regenerator unit, the extent of reaction in the reactor, reaction temperature and time of exposure to cracking conditions. To account for the fact that the activity of the catalyst can not be regenerated to that of the fresh catalyst, two types of deactivation have been postulated: A regenerable or temporary type which can be reactivated in a regenerator and nonregenerable or permanent type which can not be reactivated in a regenerator environment.

If no fresh catalyst is added to the reactor-regenerator system, the mean activity of the catalyst decreases continuously to approach zero activity or a very small activity level, which will be probably independent of the mean residence time and residence time distribution within each of the units. This is because each time the catalyst passes through the system there is some loss of activity due to permanent deactivation. However, if fresh catalyst is

continuously introduced into the reactor and an equal quantity is purged from the reactor so that the reactor inventory remains constant, and the steady state activity will be a finite non-zero value. The magnitude of the steady state value depends on the fresh catalyst feed rate, the operating conditions, the residence time distribution within the reactor and regenerator and the nominal residence time within each unit.

Mathematical Modeling

It is proposed to study the effect of regeneration on reactor catalyst activity in two stages. In the first stage, given below, a simple model has been developed for a steady state process to identify the important catalyst properties associated with regeneration. A detailed unsteady state model would be developed in the second stage which determines the activity of the catalyst in the reactor as a function of time from the time the reactor is operated. This model is thought to predict the advantages, if any, of operating the reactor in unsteady state. For example, it may be economically advantageous to operate a reactor at, say, 80% of the steady-state value when it takes considerably a long period of time to achieve a steady state. A brief description of the unsteady state process is presented in a later part of this report. In the following a mathematical model has been developed to calculate the steady-state activity of the catalyst leaving the reactor. As shown in Figure 1, the fresh catalyst feed rate is n lb/day and the spent catalyst is purged at the same flow rate. From the reactor, m lb/hr of spent catalyst is withdrawn, passed through the regenerator and recycled back to the reactor. The catalyst inventory in each unit i.e., reactor and regenerator is equal to W lb. The catalyst residence time distributions in the reactor and regenerator are denoted by $T'(t_r)$ and $T'(t_g)$, respectively. The mean activity

Figure 1. Hydrotreater-Regenerator Flow System

of the catalyst entering the reactor and that leaving the reactor are represented by $\bar{A}_i$ and $\bar{A}_0$, respectively. For simplicity, the fresh catalyst activity is taken as unity and dimensionless. For a detailed derivation of an expression for the mean catalyst activity in the reactor, see Appendix. The main equations are given below:

Step 1: Development of a relation between the mean activity of the catalyst entering the reactor ($\bar{A}_i$) and the mean activity of the catalyst leaving the reactor ($\bar{A}_0$): An activity balance over the reactor is

$$\bar{A}_0 = \bar{A}_i \tau_R \quad (\text{A.9})$$

Step 2: The mean activity of the catalyst leaving the reactor is written in terms of the distribution function, $H(\alpha)$, and permanent deactivation which has occurred in the reactor.

$$\bar{A}_0 = \bar{K}_D \left[n - \int_0^{\infty} H(\alpha) e^{-kg\alpha} d\alpha \right] \quad (\text{A.11})$$

Step 3: The mean activity of the catalyst entering the reactor is written in terms of the distribution function $H(\alpha)$ and the permanent deactivation which has occurred in the reactor.

$$(m+n)\bar{A}_i - n = m\bar{K}_D \left[t_p - t'_g \int_0^{\infty} H(\alpha) e^{-kg\alpha} d\alpha \right] \quad (\text{A.17})$$

Using the above equations, an expression is derived for the mean activity of the catalyst leaving the reactor which is independent of $\bar{A}_i$ and $H(\alpha)$:

$$\bar{A}_0 = \frac{m\bar{K}D(t_p - t'_g) + n}{\frac{m+n}{t_R} - \frac{mt'_g}{g}}$$

Using the above equation, the effects of recycle rate, permanent and temporary deactivation rate constants on the mean catalyst activity in the reactor are assessed. Typical estimates are obtained based on the operating data used in the second-stage hydrotreater at Wilsonville (i.e., fresh catalyst = 1 lb/day, reactor and regenerator catalyst inventory = 500 lb each; overall deactivation rate constant = 4 hr⁻¹). The permanent and temporary deactivation rate constants are taken as percentages of the overall deactivation rate constant.

A plot of the mean catalyst activity in the reactor ($\bar{A}_0$) as a function of recycle rate for different permanent deactivation rate constants (k_p) is given in Figure 2. For a change in the permanent deactivation rate constant from 0.005% to 0.03% of the total deactivation rate constant, the mean catalyst activity decreased from about 0.4 to about 0.08, at a recycle rate of 500 lb/hr. Thus, in general, for a fixed recycle rate, mean catalyst activity decreased with increasing permanent deactivation. For a fixed permanent deactivation, mean catalyst activity increased with increasing recycle rate.

In Figure 3, the mean catalyst activity is plotted as a function of recycle rate for different regeneration rate constants. The effect of regeneration rate constant does not seem to be significant on the catalyst activity. For example, at a recycle rate of 500 lb/hr, there is only a 15% change in the catalyst activity for a twenty fold increase in the regeneration rate constant.

Figure 2. Mean Catalyst Activity as a Function of Recycle Rate for Different Permanent Deactivation Values

Figure 3. Mean Catalyst Activity as a Function of Recycle Rate for Different Regeneration Rate Constants

Unsteady State Modeling of a Reactor-Regenerator System

In the following a theoretical model and a simulation technique are briefly described which can be used to study an unsteady state process.

Theoretical Model. Behnken et al. (1963) have developed a generalized mathematical formulation applicable for a catalytic reactor-regenerator system, a gas-solid reaction, and a crystallization process where particles grow and shrink in separate vessels. These equations can be simplified for a reactor-regenerator system. Also modifications shall be made to introduce permanent deactivation, and fresh and spent catalyst streams which are not present in the original development.

Simulation Technique

The Monte Carlo technique can provide a means to model chemical processes which are too complex for analytic solutions. Colhart et al. (1971) used this technique for a simple reactor-regenerator catalyst flow model for which analytic solutions, as explained earlier, exist. They found that reasonably accurate calculations could be made using this technique. The Monte Carlo method simply employs random chance and the convergence to a true probability in the limit. For example, if we follow a catalyst particle through a reactor-regenerator system with a properly weighted random choice each and every time there is an option, we obtain a single non-representative theory. If we repeat this n times, we obtain n random histories. As n becomes larger and larger, both the distribution of properties and average of particle properties approach the analytic values. It is planned to use this technique for solving the unsteady state equations. Presently, work is in progress in this area, and the results shall be reported as they become available.

REFERENCES

- Behnken, D. W., Horowitz, J., Katz, S., Ind. and Eng. Chem. Fundamentals, 2(3), 212, (1963).
- Beuther, H. and Schmidt, B. K., Proceedings, Sixth World Petroleum Congress, Section 3, p. 297 (1964).
- Cable, T. L., Massoth, F. E. and Thomas M. G., Fuel Proc. Tech., 4, 265 (1981).
- Colhart, J. D., Collins, D. J. and Gwyn, J. E., Chemical Engineering J., 2, 63 (1971).
- Nalitham, R. V., Tarrer, A. R., Guin, J. A., and Curtis, C. W., Ind. Eng. Chem. Process Des. Dev., to be published, 1984.
- Ocampo, A. and Schrodtt, J. T., Ind. Eng. Chem. Prod. Res. Dev., 17, 56 (1978).
- Petersen, E. E., AIChE J., 6, 488 (1960).
- Plank, C. J. and Nace, D. M., Ind. Eng. Chem., 47, 2374 (1955).
- Rudd, D. F., Can. J. of Chem. Eng., 197, October (1962).
- Sie, S. T., "Proceedings, International Symposium on Catalyst Deactivation," Delmon, B. and Froment, G. F., Ed., Elsevier Scientific Publishing Company. New York, 1980, p. 557.
- Stiegel, G. J., Polinski, L. M. and Tischer, R. E., Ind. Eng. Chem. Process Des. Deve., 21, 477 (1982).
- Stiegel, G. J., Polinski, L. M. and Tischer, R. E., Ind. Eng. Chem. Prod. Res. Dev., 22, 411 (1983).
- Wolf, E. E. and Afani, F., Catal. Rev.-Sci. Eng., 24, 329 (1982).

APPENDIX

Derivation of an Expression for the Mean Catalyst Activity in the Reactor as a Function of System Parameters

In the following, an expression is derived for the mean catalyst activity in the reactor as a function of the system parameters such as recycle rate, deactivation/regeneration rate constants etc. It is assumed that both reactor and regenerator are perfectly mixed so that the mean activity of the catalyst leaving the reactor/regenerator is the same as the mean activity of the catalyst present in the reactor/regenerator.

Step 1. The activity balance for the catalyst entering the reactor is:

steady state activity in the reactor	=	activity of one pound of fresh catalyst	+	activity of the recycle stream
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$$\frac{m+n}{\beta} \bar{A}_i = \frac{n}{\beta} + \frac{m}{\beta} \bar{K}_C \int_0^{\infty} F(\theta) R(\theta) d\theta \quad (\text{A.1})$$

where β is the weight of each particle in pounds.

The activity balance for the catalyst leaving the reactor is:

steady state activity of the catalyst in the reactor	=	activity of the fresh catalyst after passing through the reactor	+	activity of the recycle stream after passing through the reactor
---	---	---	---	--

$$\begin{aligned} \frac{m+n}{\beta} \bar{A}_o &= \frac{n}{\beta} \int_0^{\infty} R(t_r) K(t_r) T'(t_r) dt_r \\ &+ \frac{m}{\beta} \bar{K}_C \int_0^{\infty} F(\theta) \int_0^{\infty} R(\theta + t_r) T'(t_r) K(t_r) dt_r d\theta \end{aligned} \quad (\text{A.2})$$

For a well mixed reactor, the residence time distribution is given by:

$$T'(t_r) = \lambda e^{-\lambda t_r} \quad (A.3)$$

Assuming that the permanent and temporary deactivations are first order:

$$R(t_r) = e^{-k_r t_r} \quad (A.4)$$

$$K(t_r) = e^{-k_p t_r} \quad (A.5)$$

Substituting Eqs. A.3, A.4, and A.5 in Eq. A.2 we get:

$$(m+1)\bar{A}_0 = t_R + m\bar{K}_C t_R \int_0^\infty F(\theta)R(\theta)d\theta \quad (A.6)$$

Where

$$t_R = \frac{\lambda}{k_p + \lambda + k_t} \quad (A.7)$$

Eq. A.1 can be rearranged to give:

$$\int_0^\infty F(\theta)R(\theta)d\theta = \frac{(m+n)\bar{A}_i - n}{m\bar{K}_C} \quad (A.8)$$

Substituting Eq. A.8 in Eq. A.6, we get:

$$\bar{A}_0 = \bar{A}_i t_R \quad (A.9)$$

Step 2. The activity balance of the catalyst entering the regenerator is given by:

$$\begin{array}{lcl} \text{activity of} & & \text{activity of} \\ \text{the catalyst} & = & \text{catalyst} \\ \text{leaving the} & & \text{entering the} \\ \text{reactor} & & \text{regenerator} \end{array}$$

$$\frac{m}{\beta} \bar{A}_0 = \frac{m}{\beta} \bar{K}_D \int_0^\infty H(\alpha)G(\alpha)d\alpha \quad (A.10)$$

For a first order regeneration function,

$$G(\alpha) = 1 - e^{-k_g \alpha} \quad (A.1)$$

and Eq. A.10 becomes

$$\bar{A}_0 = \bar{K}_D [n - \int_0^\infty e^{-k_g \alpha} H(\alpha) d\alpha] \quad (A.12)$$

Step 3. The activity balance for the stream leaving the regenerator is given by:

steady state activity of the catalyst entering the reactor	-	activity of the fresh catalyst entering the reactor	=	steady state activity of the catalyst leaving the regenerator
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$$\frac{(m+1)}{\beta} \bar{A}_i - \frac{n}{\beta} = \frac{m}{\beta} \bar{K}_D \int_0^\infty \int_0^\infty H(\alpha) G(\alpha+t_g) K(t_g) T'(t_g) dt_g d\alpha \quad (A.13)$$

For the regenerator:

$$K(t_g) = e^{-k_p t_g} \quad (A.14)$$

$$T'(t_g) = \lambda e^{-\lambda t_g} \quad (A.15)$$

For a first order temporary regeneration function:

$$G(t_g) = 1 - e^{-k_g t_g} \quad (A.16)$$

Substituting Eqs. A.14, A.15, and A.16 into Eq. A.13 and integrating:

$$(m+n)\bar{A}_i - n = m\bar{K}_D [t'_p - t'_g \int_0^\infty H(\alpha) e^{-k_g \alpha} d\alpha] \quad (A.17)$$

$$t'_p = \frac{\lambda}{k_p + \lambda} \quad (A.18)$$

$$t'_g = \frac{\lambda}{k_p + k_g + \lambda} \quad (A.19)$$

Rewriting Eq. A.10:

$$\int_0^\infty H(\alpha) e^{-k_g \alpha} d\alpha = 1 - \frac{\bar{A}_0}{\bar{K}_D} \quad (A.20)$$

Substituting Eq. A.18 in Eq. A.15 we get:

$$(m + n) \bar{A}_i - n = m\bar{K}_D t'_p - m\bar{K}_D t'_g \left(1 - \frac{\bar{A}_0}{\bar{K}_D}\right) \quad (\text{A.21})$$

Substituting Eq. A.9 into Eq. A.21 and rewriting the equation,

$$\bar{A}_0 = \frac{m\bar{K}_D (t'_p - t'_g) + n}{\frac{m+n}{t_R} - mt_g} \quad (\text{A.22})$$

Evaluation of $\bar{K}_D$

By definition:

$\bar{K}_D$ = Mean permanent deactivation function of the stream entering the regenerator

$$= \int_0^{\infty} K(t) h'(t) dt$$

Evaluation of $h(t)$:

The residence time distribution balance for the reactor is given by the following equation:

residence time distribution of the fresh catalyst,	+	residence time distribution of the recycled catalyst after passing through the reactor	=	residence time distribution of the catalyst particles entering the regenerator
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$$\begin{aligned} \frac{n}{\beta} \int_0^t T'(t_r) dr + \frac{m}{\beta} \int_0^t F_1(t - t_r) T'(t_r) dr \\ = H_1(t_g) \frac{(m+n)}{\beta} \end{aligned} \quad (\text{A.23})$$

where if n/β tagged particles are fed continuously to the reactor then at any time t we have:

$F(t)$ = fraction of tagged particles in the recycle stream

$h(t)$ = fraction of tagged particles in the stream going to the regenerator

Similarly for the regenerator:

$$\frac{(m+n)}{\beta} \int_0^t H_1(t - t_g) T'(t_g) dt = F_1(t_g) \frac{(m+n)}{\beta} \quad (A.24)$$

Taking the Laplace transform of Eqs. A.23 and A.24:

$$(m+n) h(s) = \frac{nt_R(s)}{s} + m f(s) t_R(s) \quad (A.25)$$

$$f(s) = h(s) t_g(s) \quad (A.26)$$

Where $h(s)$, $f(s)$, $t_R(s)$, $t_g(s)$ represent the Laplace transforms of the corresponding functions. Solving Eqs. A.25 and A.26 for $h(s)$ gives

$$h(s) = \frac{nt_R(s)/s}{-mt_g(s)t_R(s) + (m+n)} \quad (A.27)$$

Now $h'(t) = L^{-1} [h'(s)]$

Where $h'(s) = s h(s)$

$$h'(s) = \frac{nt_R(s)}{(m+n) - mt_R(s)t_g(s)} \quad (A.28)$$

Substituting $t_R(s)$, $t_g(s)$ (the Laplace transforms of $T'(\tau_r)$, $T'(\tau_g)$) into Eq. A.28:

$$h'(s) = \frac{n\lambda}{m+n} \frac{s + \lambda}{(s + \lambda)^2 - m\lambda^2}$$

$$\text{thus } h'(t) = \frac{n\lambda}{m+n} e^{-\lambda t} \text{Cosh} \left(\frac{m}{m+n} \right)^{1/2} \lambda t \quad (A.29)$$

Evaluating $\bar{K}_D$:

$$\bar{K}_D = \int_0^{\infty} k(t) h'(t) dt \quad (A.30)$$

For a first order permanent deactivation:

$$k(t) = e^{-k_p t} \quad (A.31)$$

so,

$$\bar{K}_D = \frac{n\lambda}{(m+n)} \frac{(k_p + \lambda)}{(k_p + \lambda - b)(k_p + \lambda + b)} \quad (A.32)$$

where:

$$b = \frac{\sqrt{m}}{\sqrt{m+n}} \lambda$$

Thus, the mean activity of the catalyst in the reactor is given by:

$$\bar{A}_0 = \frac{(m\bar{K}_D (t_p - t_g) + n) t_R}{(m+n) - m t_g t_R}$$

where:

$$\bar{K}_D = \frac{n\lambda}{m+1} \frac{k_p + \lambda}{(k_p + \lambda - b)(k_p + \lambda + b)}$$

$$b = \frac{\sqrt{m}}{\sqrt{m+n}} \lambda$$

$$t_g = \frac{\lambda}{k_p + k_g + \lambda}$$

$$t_R = \frac{\lambda}{k_p + k_r + \lambda}$$

$$t_p = \frac{\lambda}{k_p + \lambda}$$

$$\lambda = \frac{m + n}{24w_R}$$

Nomenclature

- $\bar{A}_i$ = Mean activity of the catalyst entering the reactor
 $\bar{A}_0$ = Mean activity of the catalyst leaving the reactor
 $F(\theta)$ = Age distribution function in the reactor feed
 $f(t)$ = Fraction of particles leaving the regenerator having entered the system at time t or less
 $G(\alpha)$ = Temporary regeneration function
 $h'(t)$ = Time derivative of the fraction of particles leaving the reactor having entered the system at time t or less
 $H(\alpha)$ = Age distribution function in the regenerator feed
 $\bar{K}_C$ = Mean permanent deactivation in the recycle feed to the reactor
 $\bar{K}_D$ = Mean Permanent deactivation in the feed to the regenerator
 $K(t_r)$ = Permanent deactivation function in the reactor
 k_d = Total deactivation rate constant, $k_p + k_t$, hr^{-1}
 k_t = Temporary deactivation rate constant, hr^{-1}
 k_y = Regeneration rate constant, hr^{-1}
 m = Recycle rate, lb/day
 n = Fresh catalyst feed rate, lb/day
 k_p = Permanent deactivation rate constant, hr^{-1}
 $R(t_r)$ = Temporary deactivation function in the reactor
 s = Laplace transform variable
 t'_g = $\lambda / (k_p + k_g + \lambda)$
 t_g = Time in regenerator, hr
 t'_p = $\lambda / (k_p + \lambda)$
 t_r = Time in the reactor, hr
 t_R = $\lambda / (k_p + k_y + \lambda)$
 $T'(t)$ = Residence time distribution function where $\int_0^\infty T'(t) dt = 1$

W = Catalyst inventory in reactor/regenerator, lb
 λ = 1/Residence time in reactor (/regenerator)
 β = Weight of one catalyst particle
 α = Catalyst age in the regenerator
 θ = Catalyst age in the reactor feed

Subscripts

r = Reactor
 g = Regenerator
 p = Permanent deactivation
 i = Reactor inlet
 o = Reactor outlet
 C = Point C in Figure 1
 D = Point D in Figure 1

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