

# CONTINUOUS-DISTRIBUTION KINETIC MODEL FOR MACROMOLECULAR CONVERSION: ASPHALTENE AND POLYMER

Yoichi Kodera, Yoshiki Sato, Tohru Kamo  
National Inst. for Resources & Environment, AIST  
16-3 Onogawa, Tsukuba, Ibaraki, 305-8569, Japan

**KEYWORDS:** continuous-distribution kinetics, asphaltene, polymer

## ABSTRACT

One of the important purposes of macromolecular processing is to lower its molecular weight in cases of heavy oil processing or of feedstock recycling of plastic wastes. Molecular-weight distributions (MWDs) of macromolecular feedstocks and the reaction products at the early stage of conversion continuously span wide ranges of molecular weights. Continuous-distribution analysis is a convenient method to evaluate macromolecular conversion based on time-dependent changes of MWDs of reaction mixtures, which are readily monitored by HPLC-GPC. Kinetic models of macromolecular conversion are derived from simplified reaction schemes to interpret experimental results giving kinetic parameters, rate of conversion and activation energy. The kinetic modeling is useful to the evaluation of reaction conditions of processing regarding rate of conversion. In this presentation, kinetic models are proposed to interpret asphaltene hydrocracking and polymer degradation of polyolefin and phenolic (resole) resin. Details of experimental results will be discussed in the presentation.

## INTRODUCTION

We have been studied asphaltene hydrocracking to improve heavy oil processing [1]. The similar experimental strategy is effective on phenolic resin degradation using tetralin or co-processed polystyrene acting as a hydrogen donor [2]. Kinetic models by continuous-distribution kinetics have been proposed. In this presentation, rate of reaction is defined as a rate of increase or decrease of molar concentration of chemical species. For macromolecules, the rate are given by moment method using time-dependent changes of MWDs. Mathematical model using continuous-distribution kinetics expresses macromolecular conversion by simplified schemes at the point of MW-lowering and is useful for evaluation of the reaction conditions.

Many kinetic models have been proposed based on lumping or continuous function of measurable properties. Rice-Herzfeld and the derived mechanism are quite useful for the kinetic analysis for petroleum processing. Recently, a general kinetic model for polymer degradation based on continuous-distribution kinetics using simplified schemes of radical mechanism was reported [3,4]. This model is illustrating kinetics of polymer (especially, polyolefin) degradation and polymerization based on reversible radical-chain reaction. However, reaction mechanism is sometimes different in the reaction of each substrate due to the nature of chemical structures. The major difference of kinetic models for each substrate are derived from the amounts of hydrocarbon chains which undergo  $\beta$ -scission promoting radical chain reaction. Such chain reaction have a minor role in the macromolecular conversion such as asphaltene hydrocracking and phenolic resin degradation. The absence of the radical chain reaction at thermal treatment is a general property of thermoset plastics.

We propose kinetic models for different types of macromolecular feedstocks, i.e., phenolic resin (resole resin) with aromatic matrix, polyolefins with linear main chains of hydrocarbons, and asphaltene with fused aromatics linked by hydrocarbon chains and hydrocarbon side-chains attached to the aromatic rings. For modeling such reactions, physical issues such as diffusion and vaporization sometimes have the significant effect in an individual reactor system. As a first step, we build general kinetic models regarding chemistry of macromolecules.

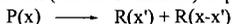
## KINETIC MODEL

Continuous-distribution kinetics consists of two technique. One is simplified notation of reaction schemes and another is moment method for converting MWDs of GPC chromatograms into amounts of moments (e. g., first moment means molar concentration). In the simplified schemes, some lumped groups of chemical species are chosen to examine the changes of amounts of moments in the function of time. A lumped group is a group of compounds which behave in the similar manner chemically and those compounds should be analytically distinguished from the other groups. For example, asphaltene from Arabian Light consists of

two types of chemical moieties, fused aromatics and hydrocarbon chains attached to the fused rings. Asphaltene hydrocracking gives asphaltene component with the lower MWs and aliphatic hydrocarbon as the major products. What we want to examine is the quantity of asphaltene component. Then, asphaltene and aliphatic hydrocarbons are the two chemical species to be described in the reaction schemes. For polyolefin degradation, chain-scission occurs along the main chain to give monomer, dimer, trimer, and oligomers. Any polymer gives oligomers via random chain-scission and some polymers give some specific products (monomer, dimer, and trimer) in high yields by specific chain-scission following to random-chain scission. Phenolic resin degradation gives only random chain-scission products. Phenols are given by the results of the random chain-scission not the reaction via  $\beta$ -scission or chain-end scission as found in polyolefin degradation.

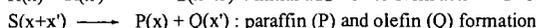
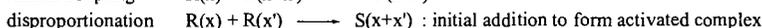
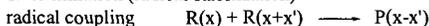
**General notation.** Rice-Herzfeld and related mechanism gave the following steps as the major radical reactions of hydrocarbons in petroleum processing. In continuous-distribution kinetics, each reaction is described as follows:

1. initiation (radical formation) of polymer P(x) with an arbitrary MW of x.



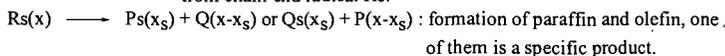
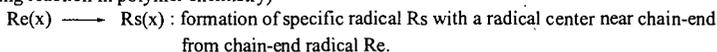
This step always gives end-radical, which has a radical center at the chain-end. The other path to form radical is radical-promoted intermolecular hydrogen-abstraction below.

2. termination (radical stabilization)



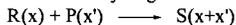
Initiation and termination step have negligible contribution to the increase of molar concentration because the major contribution is given by  $\beta$ -scission and intermolecular hydrogen-abstraction, which are the main route of radical chain reaction increasing molar concentration of the products. This concept (Long Chain Assumption) is valid only for polyolefin degradation and aliphatic components in asphaltene hydrocracking and not valid for phenolic and asphaltene components.

3. intramolecular hydrogen-abstraction by Rice-Kossiakoff mechanism (this is called as back-biting reaction in polymer chemistry)



This step is important step for the formation of specific products. End-radical is unstable to abstract a hydrogen at around fifth carbon via cyclic transition state. The resulting radical then undergo  $\beta$ -scission to give specific products, dimer or trimer.

4. Intermolecular hydrogen-abstraction



Radical also promotes intermolecular hydrogen-abstraction. This gives mostly random radical Rr(x), where radical center randomly distributes along a main chain.  $\beta$ -Scission of random radical gives the corresponding olefin and chain-end radical of random MWs.

5. Radical addition to olefins



When olefin are abundant in a reaction, radical addition is important. Some researchers report the importance of addition in liquid phase compared with that in vapor phase [5]. Using this scheme, it is possible to describe simple kinetics of polymerization [3].

Catalytic reaction involves some different mechanisms such as alkyl-group transfer and cyclization of olefin to form aromatics. These have no big change in MWs. However, one may describe lumped groups in schemes when the chemical species plays important role in the chemical or physical properties one interested in at the processing.

**Asphaltene hydrocracking.** In asphaltene hydrocracking, the conversion is evaluated at the point that decreasing rate of asphaltene component A(x). The simplified schemes shown in Schemes (A, B, C) are for the evaluation under the experimental conditions with no coking and enough supply of hydrogen[1]. Random bond-scission is assumed for the cleavage of linkages between fused-ring units (Scheme (A)), the side-chain cleavage from a fused ring (Scheme (B)), and bond-scission of aliphatic hydrocarbons (Scheme (C)) because of the possible random-distribution features of MWDs of fused-rings and linkages. Each component A(x) and P(x) separate by precipitation with hexane and is analyzed by GPC.



Polyolefin degradation is expressed as Scheme (C) due to the absence of A(x) and phenolic resin degradation is expressed as scheme (A) because of the negligible contribution of hydrocarbon linkage to the overall degradation. The detailed kinetic model for polyolefin degradation was reported in ref. [3], where reversible radical mechanism is considered.

**Phenolic resin degradation.** Presence of a hydrogen donor in phenolic resin degradation is the essential factor to proceed the degradation. One may need to know the effect of hydrogen source. The schemes including radicals are required to describe the interaction between radical intermediates and hydrogen source. Phenolic resin degradation is described as follows:



where phenolic resin is A(x) and radical is R(x).

Scheme (D) expresses radical formation ( $k_r$ ) and stabilization ( $k_R$ ). Radical formation is given by Scheme (F) and stabilization is a simplified scheme of the bimolecular reactions of a radical with a hydrogen donor such as tetralin T in Schemes (G) and (H) under the assumption of quasi-stationary state of radical [3].



Another radical formation is radical-promoted intermolecular hydrogen-abstraction, which have no contribution to the increase of concentration of radical and it is a competitive reaction to radical addition to aromatic rings. It is a determining factor to characterize phenolic resin degradation from polyolefin degradation that the resulting radical given by the hydrogen-abstraction is not expected to proceed radical chain reaction giving olefin and another radical due to the aromatic structure.

Schemes (D) and (E) gives integro-differential equations (1) and (2) according to continuous-distribution kinetics.

$$\partial a / \partial t = -k_r a(x) + k_R r(x) - k_a a(x) \int_0^\infty r(x') dx' + k_A \int_x^\infty r(x') \Omega(x, x') dx' \quad (1)$$

$$\begin{aligned} \partial r / \partial t = & k_r a(x) - k_R r(x) - k_a r(x) \int_0^\infty a(x') dx' + k_a \int_0^\infty a(x') r(x-x') dx' \\ & + k_A \int_x^\infty r(x') \Omega(x, x') dx' - k_A r(x) \end{aligned} \quad (2)$$

Applying the moment operation (McCoy [6], McCoy and Wang [7]),  $\int_x^\infty [ ] x^n dx$ , to the integro-differential equations (1) and (2) yield

$$da^{(n)} / dt = -k_r a^{(n)} + k_R r^{(n)} - k_a a^{(n)} r^{(0)} + k_A Z_{n0} r^{(n)} \quad (3)$$

$$dr^{(n)} / dt = k_r a^{(n)} - k_R r^{(n)} + k_a \left[ \sum_{j=0}^n \binom{n}{j} a^{(j)} r^{(n-j)} - a^{(0)} r^{(n)} \right] + k_A r^{(n)} (Z_{n0} + 1) \quad (4)$$

where  $Z_{n0} = 1, 1/2$ , or  $1/3$  for  $n = 0, 1$ , or  $2$ .

Zeroth moments ( $n=0$ ) are governed by the differential equations (5) and (6),

$$da^{(0)} / dt = -k_r a^{(0)} + k_R r^{(0)} - k_a a^{(0)} r^{(0)} + k_A r^{(0)} \quad (5)$$

$$dr^{(0)} / dt = k_r a^{(0)} - k_R r^{(0)} \quad (6)$$

Applying quasi-stationary state assumption (QSSA) of radical  $dr(0)/dt \approx 0$  to equation (6) gives

$$r^{(0)} = (k_r / k_R) a^{(0)} \quad (7)$$

Then,

$$da^{(0)}/dt = (k_A - k_a a^{(0)}) (k_r / k_R) a^{(0)} \quad (8)$$

Integration of equation (5) with the initial condition  $a^{(0)}(t=0) = a_0^{(0)}$  gives

$$a^{(0)} = \exp[(k_A k_r / k_R) t] / \{1/a_0^{(0)} + (k_a/k_A) [\exp[(k_A k_r / k_R) t] - 1]\} \quad (9)$$

$$a^{(0)}(t \rightarrow \infty) = k_A/k_a$$

First moments ( $n=1$ ) are given as follows:

$$da^{(1)}/dt = -k_r a^{(1)} + k_R r^{(1)} - k_a a^{(1)} r^{(0)} + (k_A/2) r^{(1)} \quad (10)$$

$$dr^{(1)}/dt = k_r a^{(1)} - k_R r^{(1)} + k_a a^{(1)} r^{(0)} - (k_A/2) r^{(1)} \quad (11)$$

The summation of first moments for polymer and radical gives

$$d[a^{(1)} + r^{(1)}]/dt = 0 \quad (12)$$

confirming the conservation of reactant polymer mass.

This is a kinetic model for resole resin in solution. Phenolic resin is its cured form with filler and other additives. Solubility of phenolic resin provide the interesting physical issues to the modeling, which will be examined in the near future.

## EXPERIMENTAL TREATMENTS FOR THE KINETICS

*Sample preparation.* Macromolecular substrates for kinetic analysis has to have a smooth distribution of MWDs because of the overlap of reaction products with the original peaks. Typically, an original resole resin contains some low MW components, which are easily removed by reprecipitation with THF and hexane. After resole resin was dissolved with THF, hexane was added with stirring. Low MW components in THF/hexane were readily removed by decantation. The residual solvent was evaporated under reduced pressure to give resole resin to be used in experiments (Fig. 1). The similar pretreatment is required in some polymers such as polystyrene.

*Analysis.* HPLC-GPC is a major apparatus to determine MWDs of reaction mixtures in this kinetics. Light scattering measurement or GC are alternative methods depending on the properties of substrates. MWDs thus obtained are converted into the corresponding amounts of moments. Mass of chemical species versus retention time of a chromatogram is calculated to give moments defined as equation (13).

$$m^{(n)} = \int_0^{\infty} x^n m(x) dx \quad (13)$$

where  $m(x)$  is molar concentration of component  $m$  in the MW range of  $[x, x + dx]$ . In GPC chromatogram using a refractive index detector have coordinates of mass concentration as intensity and retention time giving MWs. Different types of chemical species gives different intensity even if they have the same mass concentration whereas the similar chemical species of the same mass concentration gives the same peak area. For example, polystyrene samples of different MWs gives the same peak area if they are the same concentration whereas 1 g/L polystyrene and 1 g/L polyethylene give different peak area depending their refractive index. In product analysis of asphaltene hydrocracking, separate analysis is required for asphaltene components and aliphatic hydrocarbons. Asphaltene is defined as a hexane(or heptane)-insoluble component and, actually, the most parts of chemical species which have asphaltene structure do not dissolve in reaction mixtures after precipitation with hexane or heptane. Asphaltene components are analyzed by using the precipitation. MWDs of another products (aliphatic hydrocarbons) are obtained by subtracting MWDs of asphaltene components from MWDs of reaction mixtures.

Careful treatment is required to evaluate experimental results of macromolecular conversion by comparing them with a kinetic model. Some MW-standards such as asphaltene and phenolic resin are not available. Especially, it is impossible to obtain absolute MWs of asphaltene even by light scattering method due to its color. Then, molar concentration of a substrate does not change linearly with time despite to linear relation of kinetic discussion. However, we can still get the reaction rate, i.e. slope of the line, at the very early periods of the conversion and can compare the rates at different reaction conditions.

## CONCLUSION

Kinetic models by continuous-distribution kinetics for asphaltene hydrocracking, phenolic resin degradation, olefin degradation were discussed. The kinetic treatment using time-dependent changes of MWDs of reaction mixtures provide a convenient method to evaluate macromolecular conversion. Depending the nature of a macromolecule, reaction schemes should be selected carefully.

## REFERENCES

- [1] Y. Kodera, et al., Preprints of International Conference on Refinery Processes, AIChE Spring Meeting, New Orleans, March 1998, p. 321. In preparation for submission.
- [2] Sato, Y., Kodera, Y., Kamo, Y., Matsumoto, T., 7<sup>th</sup> EPF Symposium on Polymeric Materials, European Polymer Federation/Polish Chemical Society, Poland, Sept. 21, 1998. (scheduled).
- [3] Kodera, Y., McCoy, B. J., *AIChE J.*, 1997, 43, 3205.
- [4] Kodera, Y., Cha, W. S., McCoy, B. J., *Prep. Div. Fuel Chem., ACS*, 1997, 42, 1003.
- [5] Wu, G., Katsumura, Y., Matsuura, C., Ishigure, K., Kubo, J., *Ind. Eng. Chem. Res.*, 1996, 35, 4747.
- [6] McCoy, B. J., *AIChE J.*, 1993, 39, 1827.
- [7] McCoy, B. J., Wang, M., *Chem. Eng. Science*, 1994, 49, 3773.

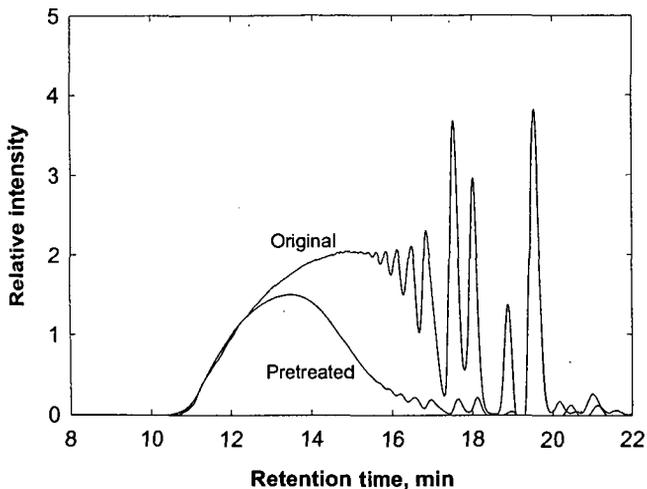


Figure 1.- RI chromatogram of resole resin before and after pretreatment  
GPC analysis was performed with a HPLC (Shimadzu LC-9A pump, RID-6A RI detector) using Polymer Laboratories GPC columns (50x7.5 mm-guard column and two 300x7.5 mm columns of 3 $\mu$ m-Mixed E) at 40 °C. THF was used as an eluent at flow rate of 1.0 mL/min.