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ACT: 519 PRESENTACION	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
LUZ CLEMENCIA DE PAEZ

Asunto: Radicación: 14-23109- -1
Trámite: 2
Evento: 1
Actuación: 519
Oficio: 4416
Folios: 6

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional	X				
Vía PCT (Fase Nacional)		Capítulo I		Capítulo II	
No. Solicitud Internacional					
Fecha de Presentación Internacional					

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Rad. N° 14-023109-00000-0000	4/Febrero/2014
Reivindicaciones:	Rad. N° 14-023109-00000-0000	4/Febrero/2014
Dibujos:	Rad. N° 14-023109-00000-0000	4/Febrero/2014

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del Capítulo Primero del Título X de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10) reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. Por lo tanto se estudiaran las reivindicaciones 1 a 11.

Título de la solicitud: “Proceso de obtención de poliuretanos a partir de aceite de palma

y poliuretanos obtenidos” (Ver. Pág. 4 del Rad. N° 14-023109-00000-0000).

El problema técnico planteado en la solicitud consiste en la necesidad de suministrar espumas de poliuretano a partir de materias primas renovables y con características deseables.

Para resolver este problema técnico, la solicitud en estudio proporciona un método de obtención de polioles a partir de aceite de palma, para su posterior polimerización a poliuretano.

El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP) C08G 018/036.

4. De la Solicitud de Patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

Las reivindicaciones 4 y 5 no son claras porque presentan una falsa dependencia a la reivindicación 1 etapa h), al indicar el tipo de catalizador, pero ningún catalizador es empleado en dicha etapa h). Se sugiere realizar la corrección necesaria.

La reivindicación 9 no es clara porque presenta una falsa dependencia a la reivindicación 1 al ser la reivindicación 9 una reivindicación de producto mientras la reivindicación 1 una reivindicación de método. Se sugiere definir el producto por sus características esenciales estructurales.

Las reivindicaciones 10 y 11 no son claras porque las expresiones “densidad”, “módulo de Young” y “esfuerzo máximo” son parámetros del poliuretano obtenido y no deberían caracterizar el compuesto solamente por sus parámetros, si es posible definirlo de otra manera. Se sugiere definirlo por sus características esenciales estructurales.

5. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud nacional, es decir, el 8 de octubre de 2008.

Consultadas las fuentes de información con que se cuenta, se encontraron los siguientes documentos que anticipan el objeto de esta solicitud.

Ítem	Documento	Título	Fecha de Publicación
D1	WO 2009/058367	“Oligomeric polyols from palm-based oils and polyurethane compositions made therefrom”	01/ Noviembre/2007
D2	WO 2007/123637	“Natural oil-derived polyester polyols and polyurethanes made therefrom”	07/Mayo/2009
D3	EP 1006133	“Polyurethane foam, process for producing the same, and foam forming composition”	21/Noviembre/2007

El documento D1¹ divulga un proceso para obtención de poliuretanos a partir de polioles obtenidos de aceite de palma (Pág. 2, Párr. 7, Pág. 5, Párr. 14, Pág. 10, Párr.31).

El documento D2² divulga un proceso para obtención de poliuretanos a partir de polioles obtenidos de aceite de palma (Pág. 2, líneas 2 a 4).

El documento D3³ divulga espumas de poliuretano con densidades de 0,100 a 1,800 g/cm³ y de 0,015 a 0,200 g/cm³ (Pág. 12, Párr. 89, Pág. 11, Párr. 77 y Párr. 79).

¹ <http://www.google.com/patents/WO2009058367A1?cl=en>

² <http://www.google.com.ar/patents/WO2007123637A1?cl=en>

³ <http://www.freepatentsonline.com/EP1006133B1.html>

6. Examen de Patentabilidad (Art 14 D486)

Novedad (Art 16 D486)

La reivindicación 9 consiste en “*Poliuretano CARACTERIZADO PORQUE se obtiene por el proceso de la reivindicación 1*” (Ver Pág. 47 del Rad. N° 14-023109-00000-0000).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D3
Poliuretano caracterizado porque se obtiene por el proceso de la reivindicación 1	La densidad del poliuretano esta entre 0,100 y 1,800 g/cm ³ o entre 0,015 y 0,200 g/cm ³ (Pág. 11, Párr. 77 y Párr. 79, Pág. 12, Párr. 89).

De acuerdo con la tabla anterior, las características esenciales del poliuretano de la reivindicación 9 habían sido divulgadas previamente en el documento D3, por lo tanto, la materia reivindicada no es nueva.

Adicionalmente se reitera que, las reivindicaciones 10 y 11 no mencionan características técnicas y/o características tangibles adicionales que puedan brindarle novedad al objeto de la reivindicación 9, puesto que se encuentran redactadas en términos de parámetros. En este caso llama la atención que con un mismo procedimiento se obtengan dos espumas de características diferentes.

Nivel inventivo (Art 18 D486)

La reivindicación 1 consiste en “*Proceso para la obtención de poliuretanos a partir de aceite de palma CARACTERIZADO PORQUE consta de los siguientes pasos*” (Ver Pág. 46 del Rad. N° 14-023109-00000-0000).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1	D2
Proceso para la obtención de poliuretanos a partir de aceite de palma caracterizado porque consta de los siguientes pasos	Proceso para obtención de poliuretanos a partir de polioles obtenidos de aceite de palma (Pág. 2, Párr. 7, Pág. 5, Párr. 14, Pág. 10, Párr.31).	Proceso para obtención de poliuretanos a partir de polioles obtenidos de aceite de palma (Pág. 2, líneas 2 a 4).
a) Mezclar una fuente de aceite de palma con ácido fórmico, en presencia de calor	Se mezcla el aceite con el ácido fórmico y el peróxido de hidrógeno (Pág. 11, Párr. 38 a Pág. 12, Pág. 39).	Se mezcla el aceite de palma con peroxiácido formado in situ entre ácido fórmico y peróxido de hidrógeno, en donde se mantiene la temperatura a 70°C (Pág. 7, línea 7 a Pág. 8, línea 32, Pág. 19, líneas 4 a 13).
b) adicionar peróxido de hidrógeno a la mezcla del paso a) y agitar		
c) Lavar el producto de reacción del paso b) con agua, a una temperatura entre 55°C y 65°C	Se lava con bicarbonato de sodio para eliminar acidez, también se adiciona agua para lavar varias veces o se combina con un tratamiento de resinas de intercambio para neutralizar, en el caso de las resinas estas intercambian iones sodio y cloruro con les hidroxilos o protones que pueda tener la solución y de esa forma neutralizar (Pág. 12, Párr. 42 a Pág. 13, Párr. 43).	Se lava con bicarbonato de sodio para eliminar acidez, también se adiciona agua para lavar varias veces o se combina con un tratamiento de resinas de intercambio para neutralizar, en el caso de las resinas estas intercambian iones sodio y cloruro con les hidroxilos o protones que pueda tener la solución y de esa forma neutralizar (Pág. 9, líneas 14 a 29).
d) Lavar el producto obtenido en el paso c) con bicarbonato de sodio al 5%		
e) Lavar el producto de reacción del paso d) con agua, a una temperatura entre 55°C y 65°C		
f) Lavar el producto obtenido en el paso e) con cloruro de sodio		

al 5%		
g) Descartar la fase acuosa obtenida en el paso f)	En el caso de usar solventes y emplear agua se generan dos fases en donde los polioles están en la fase orgánica que se seca al final (Pág. 12, Párr. 42 a Pág. 13, Párr. 43).	En el caso de usar solventes y emplear agua se generan dos fases en donde los polioles están en la fase orgánica que se seca al final (Pág. 9, líneas 14 a 29).
h) Secar al vacío la fase orgánica restante del paso f)	Se remueve al vacío los solventes orgánicos (Pág. 13, Párr. 43).	Se remueve al vacío los solventes orgánicos (Pág. 9, línea 30 a Pág. 10, línea 2).
i) Mezclar el aceite epoxidado obtenido en el paso g), con glicerina y catalizador, en presencia de calor y agitación	No se menciona	Se mezclan con glicerol y un catalizador los aceites epoxidados en donde las condiciones de apertura de los epóxidos dependen de las condiciones de agitación y relación de reactantes, siguiendo además la reacción que es de tipo exotérmica por lo que dicha reacción se realiza en caliente (Pág. 10, líneas 4 a 11 y 15, Pág. 10, línea 31, a Pág. 11, línea 2, pág. 12, líneas 4 y 5).
j) Mezclar el polioli obtenido con butanodiol	Se emplea 1,4 butanodiol para hacerlo reaccionar con el polioli (Pág. 15, Párr. 53).	No se menciona
k) Adicionar silicona y DBTL bajo agitación constante	Se adiciona DBTL como catalizador y silicona como surfactante (Pág. 23, Párr. 91)	Se adiciona DBTL como catalizador y silicona como surfactante (Pág. 17, líneas 1 a 6, líneas 24 a 28)
l) Adicionar MDI con agitación constante	Se adiciona MDI como poliisocianato (Pág. 22, Párr. 88, Pág. 24, Párr. 95).	Se adiciona MDI como poliisocianato (Pág. 15, línea 29 a Pág. 16, línea 13).
m) Obtener el poliuretano	Se obtiene un poliuretano moldeable (Pág. 2, Párr. 7, Pág. 5, Párr. 14).	Se obtiene el poliuretano (Pág. 18, líneas 4 a 14).

Los documentos D1 y D2 se consideran el estado de la técnica más cercano a la invención definida en la reivindicación 1, porque divulgan métodos donde se producen poliuretanos a partir de polioles, y los polioles a partir de aceites vegetales.

La diferencia entre la invención, definida en la reivindicación 1 y el método del documento D1 consiste en que en D1 no se menciona la mezcla del aceite epoxidado con glicerina y catalizador.

La diferencia entre la invención, definida en la reivindicación 1 y el método del documento D2 consiste en que D2 no menciona el butanodiol como materia prima en la polimerización.

El efecto técnico que logra el incluir la mezcla del aceite epoxidado con glicerina y catalizador es el de obtener a velocidades de reacción más altas un polioli con un número de hidroxilo adecuado para la síntesis de poliuretanos rígidos o semi-rígidos de forma más eficiente.

Por lo tanto, el Problema Técnico Objetivo que pretende resolver esta invención se puede formular así “¿cómo obtener a partir de aceite de palma epoxidado y a una velocidad de reacción más alta un polioli con un número de hidroxilo adecuado para la síntesis de poliuretanos rígidos o semi-rígidos de forma más eficiente?”.

Sin embargo, la etapa de la mezcla de glicerol con aceite de palma epoxidado y el catalizador para obtener un polioli ya está divulgado en el documento D2 que se refiere a la obtención de espumas mediante glicerólisis de los aceites epoxidados para la generación de polioles y su polimerización con isocianatos (Pág. 10, líneas 4 a 11 y 15,

Pág. 10, línea 31, a Pág. 11, línea 2, pág. 12, líneas 4 y 5).

En consecuencia, una persona normalmente versada en la materia incluiría la etapa de la mezcla de glicerol con aceite de palma epoxidado y el catalizador para obtener un poliol de D2 en el procedimiento para la obtención de poliuretano de la anterioridad D1, esperando con certeza lograr el método, como la de la reivindicación 1 de la solicitud, lo cual es considerado obvio y, por lo tanto, sin altura inventiva.

Asimismo, el documento D1 divulga las características de las reivindicaciones dependientes así:

Reivindicación 5: la reacción de extensión de un poliol para formar un prepolímero de alto número de hidroxilo con hidróxido de sodio como catalizador y glicerol como agente de extensión (Pág. 15, Párr. 53, Pág. 16, Párr. 64).

Reivindicación 8: la reacción de extensión del poliol para formar un prepolímero de alto número de hidroxilo con glicerol e hidróxido de sodio de 30 minutos, 1 hora con temperaturas entre 150 a 220°C (Pág. 16, Párr. 64 a Pág. 17, Párr. 66).

Asimismo, el documento D2 divulga las características de las reivindicaciones dependientes así:

Reivindicación 2: la fuente de aceite en a) es una fase oleína del aceite de palma crudo (Pág. 5, línea 30 a Pág. 6, línea 4).

Reivindicación 3: la fuente de aceite en a) es una fase oleína refinada, blanqueada y desodorizada (Pág. 5, línea 30 a Pág. 6, línea 4).

Reivindicación 6: lavado para remover acidez (Pág. 9, líneas 14 a 29).

Reivindicación 7: temperatura de 70°C después de adición del peróxido durante 1 a 9 horas para ver progreso (Pág. 19, líneas 4 a 13).

En este caso para las reivindicaciones 6 y 7 se considera que el pH 5 como punto final de lavado⁴ y las temperaturas de 45 a 55°C para la formación del epóxido⁵ no tiene nivel inventivo ya que la persona versada en la materia no aprecia efecto significativo sobre el método de obtención del poliol pues dichas condiciones se obtienen dentro de un procedimiento de optimización de procesos, lo cual se encuentra dentro de la práctica habitual de la persona versada en la materia que trabaje en la obtención de polioles y su posterior uso en la fabricación de poliuretanos.

Puesto que las reivindicaciones dependientes 2, 3 y 5 a 8 no mencionan características adicionales que hagan inventiva la solicitud, se considera que tales reivindicaciones tampoco tienen nivel inventivo.

7. Conclusión

Los requisitos de Patentabilidad de la presente Solicitud están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	WO 2009/058367	1, 5 y 8	Nivel inventivo
D2	WO 2007/123637	1 a 3, 6 y 7	Nivel inventivo
D3	EP 1006133	9 a 11	Novedad

⁴Sinadinovic-Fiser et al. Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. Journal of the american oil chemists' society. 2001. Vol. 78 (7). Pág. 726, Col. 2. Párr. 1.

⁵Purwato E. The synthesis of polyol from rice bran oil (RBO) through epoxidation and hydroxylation reactions. Thesis for master degree. School of chemical engineering. The University of Adelaide. 2010. Pág. 38, Párr. 2 a Pág. 40, Párr. 3.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir del día siguiente de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (c)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2014-04-08

Elaboró: Jorge Eduardo Cortazar Gomez
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Kinetics of *in situ* Epoxidation of Soybean Oil in Bulk Catalyzed by Ion Exchange Resin

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ABSTRACT: The kinetics of the epoxidation of soybean oil in bulk by peracetic acid formed *in situ*, in the presence of an ion exchange resin as the catalyst, was studied. The proposed kinetic model takes into consideration two side reactions of the epoxy ring opening involving the formation of hydroxy acetate and hydroxyl groups as well as the reactions of the formation of the peracid and epoxy groups. The catalytic reaction of the peracetic acid formation was characterized by adsorption of only acetic acid and peracetic acid on the active catalyst sites, and irreversible surface reaction was the overall rate-determining step. Kinetic parameters were estimated by fitting experimental data using the Marquardt method. Good agreement between the calculated and experimental data indicated that the proposed kinetic model was correct. The effect of different reaction variables on epoxidation was also discussed. The conditions for obtaining optimal epoxide yield (91% conversion, 5.99% epoxide content in product) were found to be: 0.5 mole of glacial acetic acid and 1.1 mole of hydrogen peroxide (30% aqueous solution) per mole of ethylenic unsaturation, in the presence of 5 wt% of the ion exchange resin at 75°C, over the reaction period of 8 h.

Paper no. J9753 in *JAOCs* 78, 725–731 (July 2001).

KEY WORDS: Epoxidation, ion exchange resin, *in situ*, kinetics, reaction parameters, soybean oil.

Although numerous references exist in the literature concerning the methods of epoxidation of different olefinic substrates, many fewer are concerned with the kinetics of epoxidation. The kinetics of the process depend on the reaction conditions. Epoxidation of vegetable oils can be carried out in solution or in bulk, with *in situ* (1–3) formed or preformed peracids (4–9), with homogeneous or heterogeneous catalysts.

A kinetic model for *in situ* epoxidation of anchovy oil with partially preformed peracetic acid in the presence of a resin catalyst was reported (10). In the range of the operating variables, epoxidation and ring opening were described by a pseudo first-order reaction, applying the principle of the stationary state. Two studies of the kinetics of the *in situ* epoxidation of oleic acid with hydrogen peroxide and acetic acid and of methyl esters of palm olein by performic and peracetic acid, both carried out in the presence of sulfuric acid as a

catalyst, concluded that the rate-determining step of the epoxidation process was the formation of peracetic (or performic) acid (11,12). Rangarajan *et al.* (13) reported kinetic parameters for the *in situ* epoxidation of soybean oil by peracetic acid, again in the presence of sulfuric acid as the catalyst, but treated it as a two-phase system. Significantly higher rates were obtained when heat and mass transfer limitations were removed. The proposed model also predicted the effect of the addition of an inert solvent on epoxidation.

With an acidic ion exchange resin as the catalyst for the epoxidation of vegetable oils, the porous structure of the solid catalyst and the size of the natural unsaturated triglycerides were found to minimize side reactions and thus improve selectivity (SE) (14). The presence of an inert solvent in the reaction mixture appeared also to stabilize the reaction of epoxidation and minimize side reactions, such as the opening of the epoxy ring, especially at higher temperatures (12).

Since the ion exchange resin has the same effect as a solvent, it is reasonable to assume that the epoxidation of soybean oil may be carried out in bulk with a high SE, i.e., in the absence of an inert solvent, as we did in the present work. We also carried out the epoxidation in solution to confirm our assumptions, but the emphasis was on the study of the effects of reaction variables on conversion of double bonds and epoxy yield during epoxidation of soybean oil in bulk. The reaction was conducted with peracetic acid formed *in situ* from acetic acid and hydrogen peroxide in the presence of an ion exchange resin as a catalyst. Thus, the epoxidation that we studied was a heterogeneous catalytic process characterized by the presence of a solid phase (catalyst), an aqueous phase (acetic acid, hydrogen peroxide, and water), and an oil phase. The kinetics of such a system is very complex even for the simple first-order reactions, and some assumptions such as Langmuir-Hinshelwood-Hougen-Watson postulates may help to simplify the rate equations (15).

The objective of this work was to develop, on the basis of the experimental data, a kinetic model for the heterogeneous catalytic system that describes the course of epoxidation of soybean oil in bulk, with *in situ* formed peracetic acid and an acid ion exchange catalyst. The adopted method involved the definition of possible kinetic models for different chemisorption mechanisms, their mathematical description, testing of the models by solving the system of differential equations, selection of the viable one, and comparison of the experimental data with the calculated values from the accepted model.

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EXPERIMENTAL PROCEDURES

Materials. Soybean oil with an iodine value of 130 (Hanus) was kindly supplied by "Servo Mihalj" Zrenjanin, Yugoslavia. Glacial acetic acid (>99.5%), hydrogen peroxide (30% water solution), and analytical grade benzene were used. Ion exchange resins Amberlite IR-120 from Rohm & Hass Co. (Philadelphia, PA) and Dowex 50X from Dow Chemical Co. (Midland, MI) were used in their acid form.

Methods. The epoxidation of soybean oil was carried out with peracetic acid generated *in situ*. The reaction conditions and the properties of the products are listed in Table 1. The procedure involved adding 100 g of soybean oil (0.5122 mole of ethylenic unsaturation), dissolved in glacial acetic acid and benzene (20 wt% of the soybean oil), into a 500-mL three-necked reactor, equipped with a reflux condenser, thermometer, and dropping funnel. The ion exchange resin was first added to the reactor. The amount of the applied dry ion exchange resin was expressed in percentages of the sum of the weights of the acetic acid and hydrogen peroxide used, as well as a percentage of the soybean oil weight. Cooling of the reaction mixture was maintained with the water bath and agitation with a magnetic stirrer. The temperature was kept to within $\pm 1^\circ\text{C}$, and the stirring rate was controlled (1000 rpm) so that a fine dispersion of oil was achieved. At the beginning, the mixture was heated to 50°C , and the hydrogen peroxide solution was added incrementally over a half-hour period while maintaining the reaction temperature at 50°C . Then the temperature of the reaction mixture was allowed to rise to the desired level. The reaction was followed by withdrawing and analyzing 5-mL samples of the reaction mixture at defined time intervals.

After a certain time (12 to 24 h), when the iodine value of the substrate had been reduced enough, the resin was separated from the cooled reaction mixture by filtration. If the ion exchange resin was to be reused, it was washed with ether and dried. Upon cooling, the reaction mixture separated into water and oil layers. The oil layer was washed several times with warm water ($30\text{--}35^\circ\text{C}$) until it was acid-free. The remaining traces of water and benzene (if used) were removed under a reduced pressure at $60\text{--}70^\circ\text{C}$. Every sample of the reaction mixture followed the same separation procedure described above. The products and the samples were analyzed for the iodine and epoxy oxygen (EO) values and viscosity. The Hanus method for iodine number (IO) (16) and standard HBr-acetic acid method (17) for EO content determinations were used.

RESULTS AND DISCUSSION

Effects of the reaction variables. The effect of reaction variables on the epoxidation was studied. The variables were: molar ratio of the reactants (ethylenic unsaturation of oil/acetic acid/hydrogen peroxide), the type of catalyst and catalyst concentration, temperature, and presence of an inert solvent, as well as the possibility of reusing the ion exchange resin. The values of reaction variables and product properties are shown in Table 1 only for the maximum epoxy oxygen contents ($\text{EO}_{e,m}$, where *e* indicates experimentally determined value and *m* indicates maximum value) reached in each synthesis.

The amount of hydrogen peroxide used for the epoxidation of soybean oil was always kept at 1.1 moles per mole of ethylenic unsaturation of oil. For the sample with a maximal content of EO, the concentration of unreacted hydrogen per-

TABLE 1
Values of Reaction Variables and Product Properties for the Maximal Content of Epoxy Oxygen Reached in Each Run of the *in situ* Epoxidation of Soybean Oil by Peracetic Acid in the Presence of the Ion Exchange Resin as Catalyst^a

Synthesis no.	Molar ratio Unsat./CH ₃ COOH/H ₂ O ₂			Amberlite ^b (wt%)	T (°C)	Benzene (wt%)	t (h)	Iodine number ^c (IN _e)	Conversion ^d X (%)	Epoxy oxygen ^e (EO _{e,m}) %	Yield ^f RYE (%)	Selectivity ^g (SE)	Viscosity η (mPa·s)
S1	1	1	1.1	5[4.73]	75	20	6	3.7	97.7	5.88	77.65	0.79	853.3
S2	1	5	1.1	5[10.88]	75	20	1	71.0	45.4	2.8	36.97	0.81	1462.4
S3	1	0.5	1.1	5[3.96]	75	20	8	11.0	91.5	6.02	79.48	0.87	527.7
S4	1	0.5	1.1	5[3.96]	60	—	10	17.2	86.8	5.68	74.99	0.86	444.3
S5	1	0.5	1.1	5[3.96]	30	—	24	35.0	73.1	3.70	48.85	0.67	285.6
S6	1	0.5	1.1	15[11.89]	75	—	7	4.0	96.9	6.24	82.39	0.85	577.9
S7	1	0.5	1.1	2[1.28]	75	—	12	12.3	75.2	5.01	66.15	0.88	309.5
S8	1	0.5	1.1	5[3.96]	75	—	8	11.5	91.1	5.99	79.09	0.87	522.7
S9	1	0.5	1.1	5 [3.96] (2x)	75	—	8	11.5	91.1	5.89	77.77	0.85	523.8
S10	1	0.5	1.1	5[3.96] (5x)	75	—	9	10.2	92.15	5.76	76.05	0.32	548.9
S11	1	0.5	1.1	5[3.96] ^h	75	—	9	13.4	89.7	5.94	78.42	0.87	519.5

^aFor IN₀ = 130 and EO_t = 7.574% (see below).

^bAmberlite IR-120 (Rohm & Hass Co., Philadelphia, PA). Numbers in brackets represent the concentration expressed in percentages of oil weight.

^cIodine number, determined experimentally according to Reference 16.

^dConversion X(%), conversion of double bonds as related to IN₀ (the initial IN). Calculated as $X = [(IN_0 - IN)/IN_0] \cdot 100$.

^eEO_{e,m}(%) experimentally determined maximal content of epoxy oxygen in 100 g of oil.

^fRYE (%), relative yield of epoxides, calculated as $RYE = 100 \cdot EO_e/EO_t$. EO_t is defined as the theoretical maximum content of epoxy oxygen in 100 g of oil, calculated as $EO_t = \{(IN_0/2A_j)/[100 + (IN_0/2A_j) \cdot A_0]\} \cdot A_0 \cdot 100$, where $A_j = 126.9045$ and $A_0 = 16.0000$.

^gSE, relative yields of epoxides, calculated from the conversion of double bonds, as $SE = EO_e \cdot IN_0/EO_t (IN_0 - IN)$.

^hDowex 50X (Dow Chemicals, Midland, MI).

oxide in the reaction mixture was 7.8% for the molar ratio of ethylenic unsaturation of oil/acetic acid/hydrogen peroxide = 1:0.5:1.1 (synthesis S8), coming close to the equilibrium concentration.

The effect of the acetic acid molar ratios on the epoxidation was studied by using 1, 5, and 0.5 moles of acid per mole of ethylenic unsaturation (syntheses S1, S2, and S3, respectively). Variation of both IN_e and EO_e with time is presented in Figure 1. A higher molar ratio of acetic acid to ethylenic unsaturation increased the reaction rate and the ratio of side reactions. Thus, the use of a higher molar ratio of acetic acid during *in situ* epoxidation reduced the yield of epoxy groups. The maximal yield of the epoxy groups was achieved when 0.5 mole of acetic acid per mole of ethylenic unsaturation was used.

The catalytic effect of the ion exchange resin was investigated by using 2, 5, and 15 wt% of Amberlite IR 120 (syntheses S7, S8, and S6, respectively). With an increasing concentration of the catalyst, the reaction rate and the epoxy yield increased. At the same time, the ratio of the side reactions related to the conversion of double bonds increased from 12 to 15% (SE decreased from 0.88 to 0.85). Since the maximal yield of epoxide groups, obtained with 5 wt% of the catalyst, was only 3.3% lower than those achieved with 15%, the optimal quantity of the catalyst was selected to be 5%. The effect of the catalyst concentration on the course of epoxidation is shown in Figure 2.

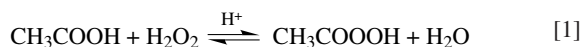
Using two strong ion exchange resins of the sulfonated polystyrene type, Amberlite IR-120 and Dowex 50X, for the epoxidation of soybean oil in bulk produced no significant difference in the maximal epoxy oxygen content (syntheses S8 and S11).

The influence of temperature (T) on the course of epoxidation was investigated by carrying out the reaction at 30, 60, and 75°C (syntheses S5, S4, and S8). Variation of IN and EO content with reaction time is displayed in Figure 3. The reac-

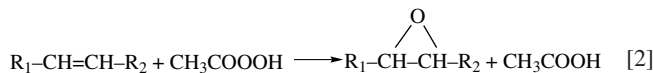
tion rate, conversion of double bonds (X), relative epoxy yield (RYE), and SE were found to increase with increasing temperature. At the highest temperature, the shortest reaction time (t) was obtained, and the maximal EO content of 5.99% was reached. Since the same relative epoxy yield but somewhat lower SE was obtained at 78°C (data not shown), the optimal temperature was selected to be 75°C.

Plots (not shown) of the change in IN and EO contents with time for syntheses S3 (with benzene) and S8 (the same parameters of epoxidation, but without benzene) showed no significant difference between the two. The presence of the solvent was not deemed necessary, since the relative epoxy yield was not significantly higher and the ratio of side reactions was the same (i.e., the SE in Table 1) when benzene was used.

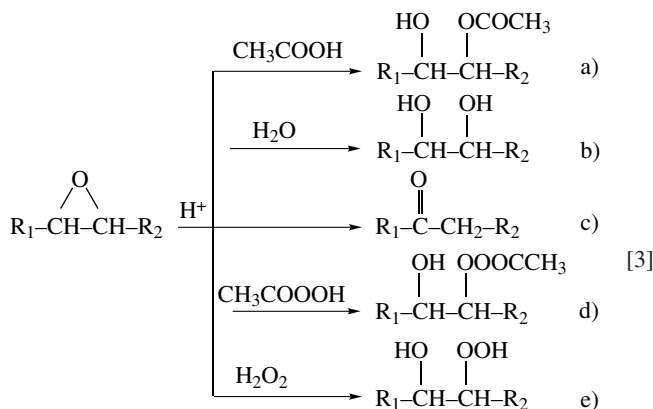
Model selection. *In situ* epoxidation of soybean oil with peracetic acid in the presence of an ion exchange resin is a heterogeneous catalytic process in which peracetic acid formation is an acid-catalyzed reaction:



whereas the main reaction involving the epoxy group formation is an uncatalyzed reaction:



The following side reactions of the epoxy ring cleavage that may take place are acid-catalyzed:



To reduce the number of model parameters, i.e., to simplify the mathematical model, which represents the system of differential equations for rates of the reactions shown above, heat and mass diffusion resistances in the system liquid–solid are usually ignored (15,18). Since the stirring was good and the epoxidation was conducted isothermally, those diffusion resistances were assumed to be negligible and the steps concerning the transport phenomena in our studies of kinetics were also ignored. Thus, the formulation of equations for the overall rates for catalyzed reactions of peracetic acid formation (reaction 1) and epoxide ring opening reactions (reactions 3) in such a case takes into consideration only the reaction on the solid catalyst, i.e., chemisorption. The reaction

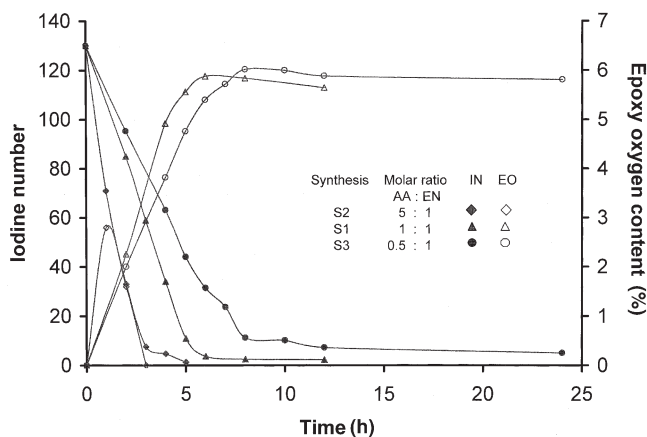


FIG. 1. Effect of different molar ratios of acetic acid (AA) to ethylenic unsaturation (EN) of oil on the *in situ* epoxidation of soybean oil in benzene (20 wt%) with 1.1 moles of 30% hydrogen peroxide at 75°C, and in the presence of 5% of Amberlite IR 120 (Rohm & Hass Co., Philadelphia, PA). IN , iodine number; EO , epoxy oxygen content.

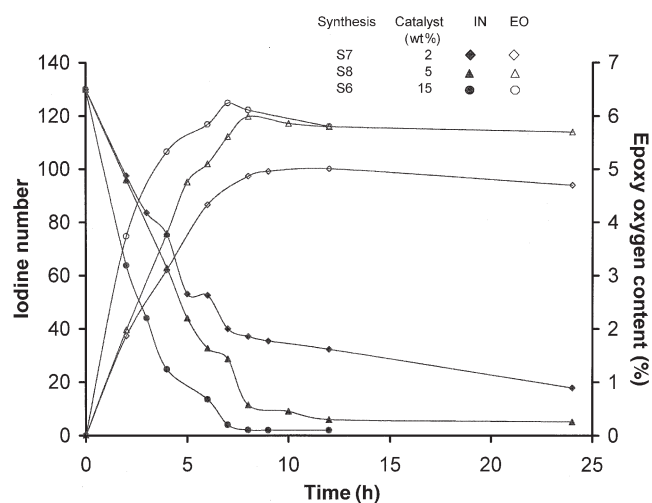


FIG. 2. Effect of the amount of catalyst on *in situ* epoxidation of soybean oil in bulk at 75°C, with molar ratio of ethylenic unsaturation of oil/acetic acid/hydrogen peroxide (30%) = 1:0.5:1.1. For abbreviations see Figure 1.

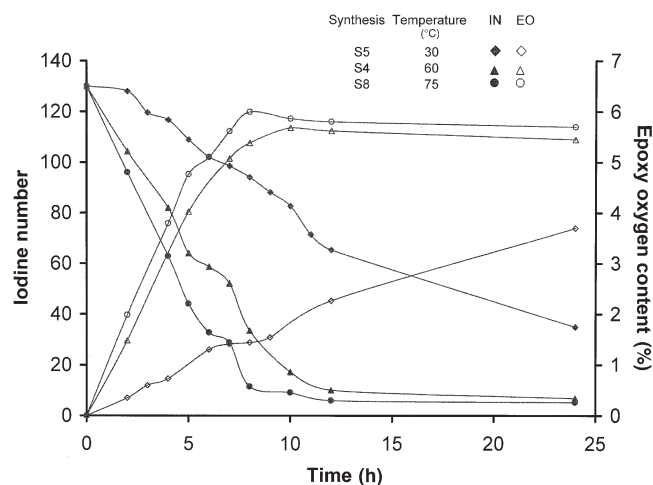


FIG. 3. Influence of temperature on *in situ* epoxidation of soybean oil in bulk with 1.1 moles of hydrogen peroxide (30%) and 0.5 mole of acetic acid in the presence of 5% of Amberlite IR 120. For abbreviations and company source, see Figure 1.

TABLE 2
Specifications of Assumptions for the Selected Kinetic Models^a

Model no.	Reaction ^b taken into consideration				Chemisorption					
					Adsorption		Reversible	Irreversible	Order	Determining step
					Dissociation					
	Homogeneous	Order	Heterogeneous	Order	Without	With				
1	1,2,3a,3b	1	—	—	—	—	—	—	—	—
2	1,2,3a,3b,3c	1	—	—	—	—	—	—	—	—
3	1,2,3a,3b	^b	—	—	—	—	—	—	—	—
4	2,3a,3b	1	1		AA, H ₂ O ₂ , PAA, H ₂ O	—	All steps	—	1	Adsorption of AA
5	2,3a,3b	1	1		AA, PAA	—	All steps	—	1	"
6	2,3a,3b	1	1		AA, PAA	—	All steps	—	^d	"
7	2,3a,3b	1	1		AA, PAA	—	Adsorption, desorption	Surface reaction	1	"
8	2,3a,3b	1	1		AA, H ₂ O ₂ , PAA, H ₂ O	—	All steps	—	1	Desorption of PAA
9	2,3a,3b	1	1		AA, PAA	—	All steps	—	1	"
10	2,3a,3b	1	1		AA, PAA	—	All steps	—	^d	"
11	2,3a,3b	1	1		AA, PAA	—	Adsorption, desorption	Surface reaction	1	"
12	2,3a,3b	1	1		AA, H ₂ O ₂ , PAA, H ₂ O	—	All steps	—	1	Surface reaction
13	2,3a,3b	1	1		AA, PAA	—	All steps	—	1	"
14	2,3a,3b	1	1		AA, PAA	—	All steps	—	^d	"
15	2,3a,3b,3c	1	1		AA, PAA	—	All steps	—	^d	"
16	2,3a–d	1	1		AA, PAA	—	All steps	—	^d	"
17	2,3a,3b	1	1		AA, PAA	—	Adsorption, desorption	Surface reaction	1	"
18	2,3a,3b	1	1		AA, PAA	—	Adsorption, desorption	Surface reaction	^d	"
19	2,3a,3b	1	1		AA	—	Adsorption	Surface reaction	1	Surface reaction
20	2	1	1		AA, H ₂ O ₂ , PAA, H ₂ O	—	All steps	—	1	Surface reaction
21	2	1	3a		EO, S	—	All steps	—	1	Surface reaction
			1		AA, PAA	—	All steps	—	1	Surface reaction
			3a		EO, S	—	All steps	—	1	Surface reaction
22	2	1	1		AA, PAA	—	Adsorption, desorption	Surface reaction	1	Surface reaction
			3a		EO, S	—	All steps	—	1	Surface reaction
			1		AA, PAA	—	All steps	—	1	Surface reaction
23	2	1	1		AA, PAA	—	All steps	—	1	Surface reaction
			3a		EO, S	—	Adsorption, desorption	Surface reaction	1	Surface reaction
			1		AA, PAA	—	All steps	—	1	Surface reaction
24	2	1	1		AA, PAA	—	All steps	—	1	Surface reaction
			3a		EO	—	Adsorption	Surface reaction	1	Surface reaction

^aAA, acetic acid; PAA, peracetic acid; EN, ethylenic unsaturation of oil; EO, epoxy oxygen; S, side reaction products.

^bReactions are enumerated in text.

^cThe assumed order for all reactions is 1, except for homogeneous reactions in model 3, where the reaction order to the left is different from that to the right.

^dSurface reaction is zero order to H₂O₂ and H₂O.

TABLE 3
Values of Calculated Kinetic Parameters^a for Models No. 13 and 17

Model No. 13		Model No. 17	
$C_i k_{sr}$	i.e., $p_1 = 2.163$	$C_i k_{sr}$	i.e., $p_1 = 2.263$
$K = (K_{AA} K_{SR})/K_{PAA}$	i.e., $p_2 = 2.048 \cdot 10^7$	K_{PAA}	i.e., $p_2 = 49.706$
k_3	i.e., $p_3 = 2.897$	k_3	i.e., $p_3 = 2.765$
k_4	i.e., $p_4 = 0.250$	k_4	i.e., $p_4 = 0.247$
k_5	i.e., $p_5 = 1.170 \cdot 10^{-4}$	k_5	i.e., $p_5 = 3.073 \cdot 10^{-4}$
K_{AA}	i.e., $p_6 = 0.9635$	K_{AA}	i.e., $p_6 = 0.973$
K_{PAA}	i.e., $p_7 = 50.151$		

^a $C_i k_{sr}$, concentration of active site per unit mass of catalyst (mol/g catalyst) $\times$ coefficient of surface reaction rate; K_{AA} , K_{PAA} , adsorption equilibrium constants; K_{SR} , equilibrium constant of surface reaction; the units for k_3 , k_4 , and k_5 , are (100 g oil)/s-mol).

proceeds on active sites of the catalyst surface in three steps: (i) adsorption of at least one of the reactants on the catalytic active site, (ii) surface chemical reaction between adsorbed atoms or molecules, or between adsorbed and not adsorbed reactants, and (iii) desorption of the products. Consequently, an overall rate equation for such a liquid–solid catalytic reaction is derived by estimating the rate equations for the individual steps, i.e., for adsorption, surface chemical reaction and desorption, and combining them to eliminate unknown surface concentrations. In this work we have adopted Langmuir-Hinshelwood-Hougen-Watson's approach for the development of the overall reaction rate equations (15). This approach reduces the number of rate coefficients (k) for individual steps and the number of equilibrium constants (K) in the overall reaction rate equation.

The next step for the simplification of the overall reaction rate equation is to assume that only one step is determining, while the other two proceed under nearly equilibrium conditions. Depending on which of the three steps controls the overall catalyzed reaction rate, it is possible, for the same assumed chemisorption mechanism, to select several kinetic expressions. If an assumption that one or all reactants/products may adsorb on active catalyst sites is also taken into consideration, the number of selected kinetic mechanisms, and thus kinetic equations for the overall catalytic reaction rate, rapidly increases.

The procedure for selecting the kinetic models in this work required choosing which reactions of the epoxidation process to consider, which are homogeneous (i.e., pseudohomogeneous) and which heterogeneous, the order of reactions, and chemisorption mechanism for heterogeneous reactions. The last-named choice refers to which reactants and/or products are adsorbed, how reactants/products are adsorbed (with or without dissociation), the reversibility or irreversibility of the steps, the order of the steps, and which step is rate-determining. Table 2 shows 24 selected kinetic models with specification of assumptions.

As was mentioned previously, the form of the kinetic equation may be different for the same chemisorption mechanism depending on which step is assumed to be rate-determining. According to the Langmuir-Hinshelwood-Hougen-Watson postulates, kinetic equations for the reactions catalyzed by a

solid are written as the combination of three groups:

$$(\text{kinetic factor})(\text{driving-force group})/(\text{adsorption group}) \quad [4]$$

The summary of expressions for these groups for various kinetic schemes is given in the literature (15). Different kinetic expressions for various assumptions concerning chemisorption resulted in different mathematical models. Each mathematical model represents a system of differential equations that mathematically describes the whole process of epoxidation. Their solution gives parameters (p_i), i.e., the concentration of active site per unit mass of catalyst, coefficients of reaction rates (k_i) and equilibrium constants (K_i) for the adsorption or desorption step, or their combinations. The inputs were experimentally determined concentrations of a reactant ($[EN]_e$) and a product ($[EO]_e$). The parameters were estimated by fitting experimental data using the Marquardt method (19). Twenty-three experimental data points (see Fig. 4) were used to fit three to eight parameters. The number of parameters varied and depended on the selected model. The Runge-Kutta method was applied for solving the system of differential equations.

Once the model parameters had been calculated, the viable model was chosen on the basis of the parameter values. Since all parameters have physical meaning, they cannot be of negative or impossible values. All selected models that gave negative values of only one parameter, or negative calculated values of reactant and/or product concentrations, were rejected. Only model Nos. 13 and 17 had positive values for all parameters and gave positive calculated values of reactant and product concentrations. Values of calculated model parameters (p_i) for both models are presented in Table 3.

In model No. 13, the high value of parameter p_2 , i.e., the equilibrium constant K , which is the consequence of the high value of the equilibrium constant of surface reaction (K_{SR} , calculated as 1.066×10^9), indicates that the surface reaction proceeds in only one direction, to the right. That is confirmed in model No. 17, where the catalytic reaction of peracetic acid for-

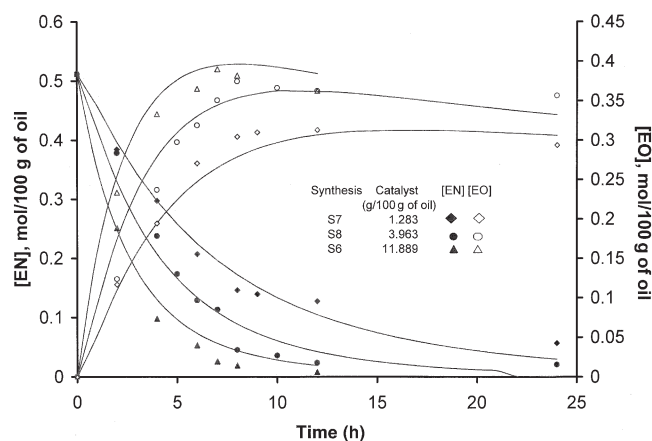
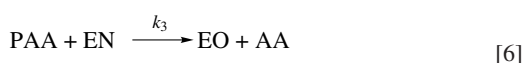
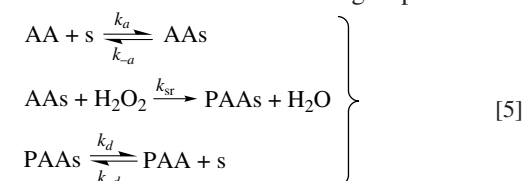


FIG. 4. Time dependence of experimentally determined (points) and calculated (solid curves) concentrations of ethylenic unsaturation of oil [EN] and epoxy oxygen [EO] for the *in situ* epoxidation of soybean oil in bulk at 75°C, with 1.1 moles of hydrogen peroxide (30%) and 0.5 mole of acetic acid, in the presence of different amounts of Amberlite IR 120. See Figure 1 for company source.

mation on the surface was supposed to be irreversible. The symbols K_{AA} and K_{PAA} refer to the adsorption equilibrium constants of acetic acid and peracetic acid, respectively. Notice that in both models the parameter p_1 is the combination of the coefficient of the surface reaction rate (k_{sr}) and the unknown concentration of active catalyst sites (C_t) where t represents "total."

Accepted model. The accepted kinetic model No. 17 assumes that in the catalytic reaction of the peracetic acid formation (1), only acetic (AA) and peracetic (PAA) acids are adsorbed on the active catalytic site(s) and that irreversible surface reaction is the overall rate-determining step:



where letter subscripts in the rate coefficients (k_i) indicate adsorption (a), surface reaction (sr), and desorption (d). AAs and PAAs describe adsorbed acetic acid (AA) and peracetic acid (PAA) on s, EN is the ethylenic unsaturation of soybean oil, EO is epoxy oxygen, and S is the product of the side reaction.

The corresponding mathematical model may be represented by the following equations:

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -\frac{M_k C_t k_{sr} K_{AA} [\text{AA}] [\text{H}_2\text{O}_2]}{1 + K_{AA} [\text{AA}] + K_{PAA} [\text{PAA}]} \quad [8]$$

$$\frac{d[\text{AA}]}{dt} = \frac{d[\text{H}_2\text{O}_2]}{dt} + k_3 [\text{PAA}] [\text{EN}] - k_4 [\text{EO}] [\text{AA}] \quad [9]$$

$$\frac{d[\text{PAA}]}{dt} = -\frac{d[\text{H}_2\text{O}_2]}{dt} - k_3 [\text{PAA}] [\text{EN}] \quad [10]$$

$$\frac{d[\text{EN}]}{dt} = -k_3 [\text{PAA}] [\text{EN}] \quad [11]$$

$$\frac{d[\text{EO}]}{dt} = k_3 [\text{PAA}] [\text{EN}] - k_4 [\text{EO}] [\text{AA}] - k_5 [\text{EO}] [\text{H}_2\text{O}] \quad [12]$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = -\frac{d[\text{H}_2\text{O}_2]}{dt} - k_5 [\text{EO}] [\text{H}_2\text{O}] \quad [13]$$

$$\frac{d[\text{S}]}{dt} = k_4 [\text{EO}] [\text{AA}] + k_5 [\text{EO}] [\text{H}_2\text{O}] \quad [14]$$

where brackets are used to define the concentration of the reactants, M_k is the catalyst-to-oil ratio, and K_{AA} and K_{PAA} are the adsorption equilibrium constants for AA and PAA, respectively.

TABLE 4

Comparison of Experimentally Determined and Calculated Values of Time, IN, and EO for Maximal Yields of Epoxide, Reached in the *in situ* Epoxidation of Soybean Oil by Peracetic Acid, in the Presence of Different Quantities of the Ion Exchange Resin, at 75°C^a

Synthesis no.	Catalyst (wt%)	t_e (h)	IN _e	EO _{e,m} (%)	t_c (h)	IN _c	EO _c (%)
S7	2	12	12.3	5.01	15	16.92	5.01
S8	5	8	11.5	5.99	10	12.87	5.80
S6	15	7	4.0	6.24	8	9.23	6.34

^aSubscript e, experimental; subscript c, calculated; subscript m, maximal; for other abbreviations see Table 1.

The calculated parameters for the accepted model No. 17 are given in Table 3. This mathematical model fits well the experimental values of the measured variables: concentrations of ethylenic unsaturation of oil [EN] and [EO]. Figure 4 illustrates the results of the epoxidation of soybean oil by *in-situ* generated peracetic acid in bulk in the presence of different concentrations of Amberlite IR 120 applied as catalyst at 75°C. It shows the time change for both the experimentally determined values ([EN]_e and [EO]_e) and the calculated ones ([EN]_c and [EO]_c), as the points and solid curves, respectively.

Table 4 shows the numerical values of the IN and EO content calculated from the accepted model (IN_c and EO_c), together with the experimentally determined ones (IN_e and EO_e), all for the attained maximal yields of EO.

Although the experimental and calculated values of the maximal content of EO do not differ by more than 3.27% (for the synthesis S8), the differences between real and predicted reaction times to reach the maximum content of EO are significant. That may be explained by the difficulty in locating a precise maximum on experimental curves (see Fig. 2). Good agreement between experimental and calculated data indicates that the proposed model No. 17 is correct. It suggests that the catalytic reaction of peracetic acid formation may be considered irreversible, since the reaction of epoxy compound formation, involving consumption of peracetic acid, is fast enough ($k_3 > C_t k_{sr}$) and the equilibrium in the reaction of peracetic acid formation shifts to the right. Small rate coefficients (k_4 and k_5 in Table 3) for both side reactions (6a and 6b) indicate that the ring opening reactions do not occur to a significant extent. This is reflected in the high values of SE in Table 1 for all S6, S7, and S8 syntheses.

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