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FACULTAD DE QUÍMICA

Síntesis no Catalítica de Biodiésel con Metanol Supercrítico en Reactor Tanque discontinuo a Partir de Aceite de Soja Refinado

Dª Pilar Olivares Carrillo

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Síntesis no Catalítica de Biodiésel con Metanol Supercrítico en Reactor Tanque Discontinuo a partir de Aceite de Soja Refinado

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1º.- Quesada, J.; Olivares, P. Supercritical Biodiesel Production from Raw Soybean Oil. *Journal of Biofuels* **1** (2010) 115-122.

2º.- Quesada-Medina, J.; Olivares-Carrillo, P. Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol. *Journal of Supercritical Fluids* **56** (2011) 56-63.

3º.- Olivares-Carrillo, P.; Quesada-Medina, J. Synthesis of biodiesel from soybean oil using supercritical methanol in a one-step catalyst-free process in batch reactor. *Journal of Supercritical Fluids* **58** (2011) 378-384.

4º.- Olivares-Carrillo, P.; Quesada-Medina, J. Thermal decomposition of fatty acid chains during the supercritical methanol transesterification of soybean oil to biodiesel. *Journal of Supercritical Fluids* **72** (2012) 52-58.

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El Dr. **D. Joaquín Quesada Medina**, Profesor Titular de Universidad en el Departamento de Ingeniería Química de la Universidad de Murcia, como Director del presente trabajo titulado "**Síntesis no catalítica de biodiésel con metanol supercrítico en reactor tanque discontinuo a partir de aceite de soja refinado**",

AUTORIZA:

La presentación de dicho trabajo por la alumna **Dña. Pilar Olivares Carrillo** como Tesis Doctoral en la modalidad de Compendio de Publicaciones ya que reúne todos los requisitos establecidos por la Universidad de Murcia, conteniendo cuatro artículos publicados en revistas internacionales de reconocido prestigio que configuran una unidad temática científica.

Y para que así conste, firmo la presente autorización en Murcia a 18 de octubre de 2012.

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Vista la solicitud presentada el día 1 de octubre de 2012, por Dª PILAR OLIVARES CARRILLO, con DNI número 48.466.157-M, sobre autorización para presentación de tesis doctoral como compendio de publicaciones con carácter previo a la tramitación de la misma en la Universidad de Murcia, le comunico que la Comisión de General de Doctorado, vistos:

- el informe previo del Presidente de la Comisión Académica del Doctorado en Ingeniería Química , responsable de la autorización de la tesis doctoral en fase de elaboración, de esta Universidad, y
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resolvió, en su sesión de 4 de octubre de 2012, **ACCEDER** a lo solicitado por el interesado pudiendo, por lo tanto, presentar su tesis doctoral en la modalidad de compendio de publicaciones.

Lo que en cumplimiento del artículo 58 de la vigente Ley 30/1992, de Régimen Jurídico de las Administraciones Públicas y del Procedimiento Administrativo Común, de 26 de noviembre, se **notifica a** Dª PILAR OLIVARES CARRILLO, significándole que contra esta resolución, que pone fin a la vía administrativa, se podrá interponer potestativamente ante el mismo órgano que la ha dictado, recurso de reposición, en el plazo de un mes a contar desde el día siguiente a su notificación, de acuerdo con lo dispuesto en el art. 116 de la citada Ley.

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Murcia, 4 de octubre de 2012
Vicerrectora de Estudios y
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Concepción Palacios Bernal

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On revient de loin. La formation bourgeoise,
l'orgueil intellectuel.
La nécessité de se réviser à tout moment.
Les liens qui subsistent.
La sentimentalité.
L'empoisonnement de la culture orientée.

Paul Vaillant-Couturier

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I. Introducción

Introducción

Actualmente la comunidad mundial ha comenzado a concienciarse seriamente sobre el calentamiento global y el uso masivo hasta ahora realizado de los combustibles fósiles. Para mitigar estos problemas es necesario encontrar fuentes de energía sostenibles y respetuosas con el medio ambiente que ayuden a reducir el consumo de los combustibles fósiles o incluso a sustituirlos completamente. Debido al actual modelo tecnológico, político y de desarrollo logístico basado en las fuentes de energía conocidas hasta hoy, las investigaciones se están centrando en la búsqueda de alternativas compatibles con las actuales aplicaciones, en especial con el sector del transporte.

El biodiésel es uno de los mejores candidatos que cumplen con los criterios de sostenibilidad, no sólo porque su producción tenga menos impacto ambiental sino porque además es biodegradable y no tóxico. Además, la posibilidad de descentralizar la producción de combustibles, el nuevo impulso que se está dando a la agricultura (especialmente en países en desarrollo), la creación de nuevos puestos de trabajo, el sueño de la soberanía energética, la naturaleza renovable de los biocombustibles, su balance nulo de emisiones de efecto invernadero si se usa adecuadamente y la significativa reducción de emisiones contaminantes durante su combustión, convierten al biodiésel en un producto acorde con el paradigma vigente del desarrollo sostenible. Este biocombustible ofrece globalmente muchas posibilidades en un mundo cada vez más exigente energética y ambientalmente. Este reto obliga a trabajar de modo más intenso, buscando espacios, materias primas y procesos que hagan esta alternativa más viable social y económicamente.

El proceso de producción de biodiésel se basa en la reacción de transesterificación de los triglicéridos presentes en los aceites vegetales y las grasas animales con alcoholes de bajo peso molecular (entre 1 y 5 átomos de carbono). El alcohol más utilizado actualmente es el metanol debido a su menor precio y mayor reactividad, aunque también está aumentando el uso del etanol ya que puede obtenerse a partir de recursos renovables.

La transesterificación suele ser catalizada por bases [1], ácidos [2] o enzimas [3], siendo la catálisis básica homogénea la técnica más ampliamente utilizada en la industria ya que es mucho más rápida y requiere menor cantidad de catalizador [4].

Sin embargo, el uso de esta última técnica no es adecuado cuando el aceite presenta contenidos en agua y ácidos grasos libres superiores a 0.06% y 0.5%, respectivamente, ya que se producen reacciones de saponificación que pueden dar lugar a un biodiésel de peor calidad [5,6]. Para el tratamiento de materias primas ácidas se han propuesto diferentes soluciones: (i) pre-neutralización de los ácidos grasos libres (fácil de hacer pero da lugar a un menor rendimiento si los jabones no se reciclan), (ii) pre-esterificación de los ácidos grasos libres (con metanol o glicerina) catalizada por ácidos fuertes, seguida de una transesterificación en medio alcalino, y (iii) esterificación catalizada completamente por ácidos.

Una alternativa a estos procesos es llevar a cabo la transesterificación con metanol supercrítico ya que no necesita estrictamente el empleo de catalizadores, aunque requiere un mayor exceso de metanol para obtener rendimientos de biodiésel elevados. La presencia de ácidos grasos libres no interfiere el proceso supercrítico al producirse simultáneamente la transesterificación de los triglicéridos y la esterificación de los ácidos grasos libres, sin formación alguna de jabones, mientras que el agua, que perjudicaba en gran medida la transesterificación convencional, favorece en este caso el rendimiento de la reacción [7,8]. Además, como durante la reacción supercrítica no se requiere el uso de catalizadores, no son necesarias etapas posteriores de lavado para su eliminación. En condiciones supercríticas el metanol y el aceite son miscibles (sistema homogéneo), de manera que se favorece el encuentro entre las especies y, por tanto, la reacción al no existir transferencia de masa en la interfase que limite la velocidad de reacción.

La reacción de transesterificación se da en tres etapas consecutivas y reversibles [9,10], convirtiéndose sucesivamente los triglicéridos en diglicéridos, monoglicéridos y, finalmente, en glicerina, con liberación de una molécula de éster alquílico en cada etapa. La transformación de los monoglicéridos es la etapa más lenta del proceso ya que estos compuestos son los más estables [11]. El producto obtenido tras la reacción consiste generalmente en una mezcla de ésteres metílicos de ácidos grasos (biodiésel), glicerina, alcohol, monoglicéridos, diglicéridos, triglicéridos y compuestos de descomposición térmica. La presencia de monoglicéridos en el biodiésel obtenido produce turbidez, de manera que la norma UNE-EN 14214 limita su contenido a un máximo de 0.8% en peso. En general, las impurezas elevan los puntos de nube y fluidez del biodiésel, con lo que esta norma también limita el contenido en diglicéridos y triglicéridos hasta un máximo de 0.2% en peso cada uno.

En la literatura científica existe una aparente contradicción en cuanto a las condiciones de reacción necesarias para conseguir el mayor rendimiento de biodiésel durante la metanólisis supercrítica. Las principales variables que afectan a la reacción son la temperatura, la relación molar metanol/aceite y el tiempo de reacción o tiempo espacial. Otras variables influyentes son la presión de operación (directamente relacionada con la temperatura de reacción y el volumen de llenado del reactor en reactores discontinuos) y la velocidad de agitación del medio. La temperatura y el tiempo de reacción óptimos se suelen encontrar entre 280 y 400ºC, y entre 4 y 30 min, respectivamente, en función del tipo de reactor y aceite utilizados [12,13], existiendo, por el contrario, unanimidad en cuanto a la mejor relación molar metanol/aceite, que se haya en el rango 40:1-45:1 [14-17]. El uso de estas condiciones de reacción [18] puede dar lugar a la descomposición térmica de: (i) los triglicéridos presentes en el aceite, (ii) los ésteres metílicos de ácido graso generados durante la reacción, (iii) los productos intermedios de reacción (monoglicéridos y diglicéridos), y (iv) el principal subproducto del proceso (glicerina), lo que da lugar en la mayoría de los casos a menores rendimientos de biodiésel de los esperados [13].

Una de las principales preocupaciones durante la reacción supercrítica es la estabilidad térmica de los ésteres metílicos generados. Kusdiana y Saka fueron los primeros investigadores que en el año 2001 indicaron la descomposición térmica de los ésteres metílicos de ácido graso durante la reacción supercrítica. Estos investigadores observaron que los ésteres metílicos insaturados y saturados empezaban a descomponer a 350 y 400ºC, respectivamente [19,20]. Posteriormente, He y col. [21] señalaron que los ésteres metílicos poliinsaturados (que contienen dos o más dobles enlaces: linoleato y linolenato de metilo) descomponían por encima de 300ºC, mientras que Shin y col. [22] demostraron que la degradación se producía a partir de 330ºC. Además, Imahara y col. [23] observaron que los ésteres metílicos saturados (palmitato y estearato de metilo) eran estables hasta los 300ºC, volviéndose inestables a 350ºC, mientras que Shin y col. [22] especificaron que (i) el palmitato de metilo permanecía prácticamente estable hasta los 400ºC y (ii) el estearato de metilo era estable por debajo de 350ºC, descomponiendo ligeramente a 375ºC. En el caso del oleato de metilo (principal éster metílico monoinsaturado generado a partir de la mayoría de los aceites vegetales), éste comienza a ser inestable a 375ºC [22]. Por lo tanto, se puede concluir que cuanto más corta y más saturada es la cadena grasa, mayor es su estabilidad térmica en metanol supercrítico.

Entre las reacciones indeseables de descomposición térmica de las cadenas grasas que se pueden producir durante el proceso supercrítico a temperaturas superiores a 300-325ºC se encuentran: (i) la oligomerización y polimerización de los triglicéridos y ésteres metílicos insaturados generados [24], (ii) la dimerización lineal de los ésteres metílicos monoinsaturados (con formación de una estructura acíclica de los dímeros) y poliinsaturados (con formación de una mezcla de dímeros monocíclicos y cíclicos de seis miembros) [25], (iii) la isomerización estructural, geométrica y posicional de los dobles enlaces olefínicos presentes en las cadenas grasas insaturadas, básicamente isomerización *cis/trans* [22,23,26], (iv) la hidrogenación de los dobles enlaces olefínicos anteriormente mencionados [22], (v) el craqueo térmico de las cadenas grasas saturadas (con formación de ésteres metílicos de menor peso molecular, 1-alquenos y n-alcanos) [22] y (vi) el craqueo térmico de las cadenas grasas insaturadas (con formación de ésteres metílicos saturados e insaturados en el rango C8-C14, que surgen de la ruptura de los dobles enlaces olefínicos) [22,26,27].

La glicerina también descompone durante el proceso supercrítico, dando lugar a compuestos de bajo peso molecular (acroleína, acetaldehído, ácido acético, alcoholes tales como propanol, etc.), poligliceroles (fundamentalmente compuestos de tipo diglicerol), metil glicerol éteres (mono-, di- o tri-metil glicerol) y agua [27-29]. El agua generada puede reaccionar posteriormente con los glicéridos de la mezcla de reacción para formar ácidos grasos libres, aumentando así la acidez del producto; a tiempos de reacción más largos estos ácidos se pueden transformar de nuevo en ésteres metílicos [28].

Diferentes autores [27,30-33] han observado que si el proceso supercrítico se lleva a cabo a temperaturas y presiones más altas (350-450ºC, 100-400 bar) durante tiempos de reacción más cortos (3-10 min) y usando relaciones molares metanol/aceite moderadas (3:1-12:1), entonces toda la glicerina generada descompone, dando lugar a los compuestos indicados anteriormente. Estos compuestos se incorporan al biodiésel generado, formando una única fase líquida homogénea, lo que supone un incremento de más del 10% de la cantidad de combustible producido [28,30,31]. A pesar de que en estas condiciones de reacción se produce la descomposición térmica de los ésteres metílicos, el biodiésel obtenido es de buena calidad, cumpliendo con los contenidos de glicerina libre y total establecidos por la norma UNE-EN 14214 [27]; además, durante el proceso no se generan compuestos gaseosos.

Éteres derivados de la glicerina, tales como el terbutil glicerol éter, que es soluble en biodiésel [34] y se genera durante el proceso supercrítico, influyen positivamente en la calidad del producto final, reduciendo la viscosidad y mejorando las propiedades de flujo en frío del biodiésel [23,31,32]. Otros éteres, tales como 3-metoxi-1,2-propanodiol, dimetoximetano, 2,2-dimetoxipropano y 3-etoxi-1,2-propanodiol, que se obtienen durante la reacción de la glicerina con metanol a 270ºC/10 MPa, pueden ser utilizados como aditivos oxigenados del combustible diésel para reducir la formación de hollín en los motores [35,36].

Los productos de descomposición térmica de los ésteres metílicos, fundamentalmente los ésteres metílicos de bajo peso molecular, también parecen mejorar la viscosidad y las propiedades de flujo en frío del biodiésel [30], de manera que es perfectamente tolerable un cierto grado de descomposición de las cadenas grasas. Sin embargo, otras propiedades importantes del biodiésel podrían verse algo afectadas negativamente. Así, el índice de cetano podría disminuir ligeramente debido a la descomposición de los ésteres metílicos poliinsaturados, lo que da lugar a la formación de ésteres más pequeños y estables [33]. Además, el punto de inflamación también puede disminuir ligeramente, mientras que la acidez podría aumentar [33]. En cualquier caso, los valores de la mayoría de las propiedades del biodiésel producido en condiciones supercríticas severas se encuentran dentro de los rangos especificados por las normas internacionales para biodiésel. En la actualidad aún no se ha realizado un test ASTM completo, incluyendo un test de emisiones y del rendimiento del motor, para evaluar la calidad del biofuel obtenido en condiciones supercríticas severas.

II. Objetivos

Objetivos

El objetivo general de esta tesis doctoral es el estudio de la reacción de transesterificación de aceite de soja refinado con metanol en condiciones supercríticas en reactor tanque discontinuo para la obtención de biodiésel. Para ello, los objetivos específicos de esta investigación son los que se enumeran a continuación:

1. Diseño de un reactor tanque discontinuo que permita trabajar a temperaturas y presiones de hasta 400ºC y 500 bar, respectivamente.
2. Puesta a punto de métodos analíticos para la determinación de: (i) monoglicéridos, diglicéridos y triglicéridos por cromatografía de permeación en gel (GPC), (ii) ésteres metílicos por cromatografía de gases (GC/FID) según la norma UNE-EN 14103:2003, (iii) glicerina libre, monoglicéridos, diglicéridos y triglicéridos por cromatografía de gases (GC/FID) según la norma UNE-EN 14105:2003 y (iv) el grado de descomposición térmica de las cadenas de ácido graso por cromatografía de gases (GC/FID) tras la aplicación del método oficial Ce 2-66 de la AOCS.
3. Estudio detallado de la conversión de triglicéridos y del rendimiento de biodiésel, glicerina, productos intermedios (monoglicéridos y diglicéridos) y principales ésteres metílicos saturados e insaturados generados durante la síntesis de biodiésel con metanol supercrítico a temperaturas, tiempos de reacción y relaciones molares metanol/aceite comprendidos en los intervalos 250-350ºC, 15-90 min y 13:1-53:1, respectivamente.
4. Determinación del grado de descomposición térmica de las cadenas de ácido graso en las condiciones de reacción ensayadas.

III. Materiales y Métodos

Materiales y Métodos

Materiales

Se utilizó un aceite de soja comercial refinado, que fue suministrado por Lesieur Cristal (Roche Noires, Casablanca, Marruecos), cuya composición en ácidos grasos (% mol) fue: palmítico (C16:0), 11.1; esteárico (C18:0), 3.7; oleico (C18:1), 24.4; linoleico (C18:2), 53.1; linolénico (C18:3), 7.2; y otros, 0.5.

También se empleó metanol anhidro para la reacción, que fue suministrado por Panreac Química, S.A.U. (Castellar del Vallès, Barcelona, España). Además, se usaron como estándares heptadecanoato de metilo, 1,2,4-butanotriol, 1,2,3-tricaproilglicerol (tricaprina), monooleina, dioleina, trioleina, monolinoleina, dilinoleina, trilinoleina y glicerina, que fueron proporcionados por Sigma–Aldrich (Tres Cantos, Madrid, España).

Método de trabajo

La reacción se llevó a cabo en un reactor discontinuo cilíndrico construido en acero inoxidable A310 de 84 ml de capacidad y certificado a una presión de 100 MPa, en el que inicialmente se introdujeron el aceite y el metanol. Una vez cargado el reactor, éste se sumergió en un baño de sales fundidas (mezcla eutéctica de punto de fusión mínimo, 156ºC, constituida por un 56% de KNO_3 y un 44% de $NaNO_2$) previamente calentado a la temperatura deseada, alcanzándose la temperatura de reacción en unos 10 min. El reactor se agitó a 70 rpm durante la reacción. El tiempo de reacción empezó a contabilizarse desde el momento en que el reactor se introdujo en el baño de sales fundidas. La reacción se detuvo por inmersión del reactor en baño de agua. El tiempo necesario para enfriar el reactor (hasta 90 y 45ºC) fue corto (alrededor de 90 y 150 s, respectivamente). El producto obtenido tras el proceso se evaporó a vacío en rotavapor a 52ºC durante 2 h para eliminar su contenido de metanol y acetona de lavado del reactor. Finalmente, el producto se almacenó en frigorífico antes de ser analizado.

Métodos analíticos

La reacción fue monitorizada por cromatografía de gases (GC/FID) para determinar el contenido de glicéridos (monoglicéridos, diglicéridos y triglicéridos), glicerina libre y ésteres metílicos de ácido graso en las muestras de reacción. También se usó en algunos casos la cromatografía de permeación en gel (GPC) para el análisis de monoglicéridos, diglicéridos y triglicéridos con el fin de contrastar los resultados. Además, se determinó el grado de descomposición térmica de las cadenas grasas según el método descrito por Vieitez y col. [37] tras el tratamiento de las muestras de acuerdo con el método oficial Ce 2–66 de la AOCS, que en última instancia implicaba un análisis por cromatografía de gases.

Los equipos de análisis consistieron en: (i) un cromatógrafo de gases 3900 de Varian equipado con un inyector automático CP 8400 de Varian y acoplado a un detector de ionización de llama (FID), y (ii) un cromatógrafo de líquidos LC-Module I de Waters provisto de un detector de índice de refracción (RI) 2414 de Waters. La adquisición y el tratamiento de datos se llevaron a cabo en ambos equipos mediante el software Galaxie de Varian.

Análisis de glicéridos y glicerina libre

El análisis de monoglicéridos, diglicéridos, triglicéridos y glicerina se realizó según la norma UNE-EN 14105:2003. El principio del método se basa en la transformación de los glicéridos y la glicerina en sus respectivos derivados sililados, que son más volátiles. La sililación se llevó a cabo usando N-metil-N-(trimetilsilil) trifluoroacetamida (MSTFA) y en presencia de piridina. El método requiere el uso de dos disoluciones de patrón interno: (a) nº 1, obtenida disolviendo 50 mg de 1,2,4-butanotriol en 50 ml de piridina en matraz aforado; y (b) nº 2, obtenida disolviendo 80 mg de 1,2,3-tricaproilglicerol (tricaprina) en 10 ml de piridina en matraz aforado.

Se pesaron 100 mg de muestra en un vial de 10 ml y, posteriormente, se añadieron 80 µl de disolución estándar nº 1, 100 µl de disolución estándar nº 2 y 100 µl de MSTFA, evitando el contacto con la humedad. A continuación, se cerró el vial con fuerza, se agitó vigorosamente y se dejó reposar durante 15 min a temperatura ambiente. Finalmente, se añadieron 8 ml de heptano y se inyectó una alícuota de 2 µl en el cromatógrafo de gases.

El cromatógrafo estaba provisto de una columna capilar FactorFour VF-5ht (10 m x 0.32 mm, 0.1 µm de espesor de película). Se usó helio como gas portador a un caudal de 1 ml/min, empleando una relación de split de 1:70. La rampa de temperatura en el horno fue: 1 min a 50ºC, 15ºC/min hasta 180ºC, 7ºC/min hasta 230ºC, 10ºC/min hasta 370ºC y 5 min a 370ºC. La temperatura del detector fue de 380ºC y la del inyector de 280ºC.

En algunas ocasiones se utilizó también la GPC para el análisis de los glicéridos, adaptando el método descrito por Arzamendi y col. [38]. En este caso el equipo estaba provisto de dos columnas Styragel conectadas en serie (HR1 y HR0.5, cada una de 7.8 x 300 mm y 5 µm). Las medidas se llevaron a cabo en condiciones isocráticas y a temperatura ambiente, usando tetrahidrofurano (THF) como fase móvil a un caudal de 0.9 ml/min. El volumen de inyección fue de 50 µl y el tiempo total de elución del cromatograma de 30 min. Se obtuvieron curvas de calibrado para mezclas monooleina-monolinoleina, dioleina-dilinoleina y trioleina-trilinoleina, que se usaron para convertir las áreas cromatográficas integradas en concentraciones másicas.

Análisis de ésteres metílicos

La determinación de los ésteres metílicos se llevó a cabo según la norma UNE-EN 14103:2003. Para ello, se disolvió una muestra de 250 mg en 5 ml de disolución estándar (preparada en un matraz aforado por disolución de 500 mg de heptadecanoato de metilo en 50 ml de heptano) en un vial de 10 ml. A continuación, se cerró el vial con tapón de teflón y se agitó vigorosamente. Finalmente, se inyectaron 2 µl de la disolución obtenida en el cromatógrafo de gases.

El equipo disponía de una columna capilar CP-Wax 52-CB (30 m x 0.32 mm, 0.25 µm de espesor de película). Se utilizó helio como gas portador a un caudal de 1 ml/min, siendo el modo de inyección con split (relación de split 1:50). La temperatura del horno se mantuvo siempre a 210ºC, y la del inyector y detector a 250ºC.

Determinación del grado de descomposición térmica de cadenas grasas

Las muestras fueron tratadas con BF_3/MeOH según el método oficial Ce 2-66 de la American Oil Chemists' Society (AOCS) con el fin de transformar los glicéridos y ácidos grasos libres en sus correspondientes ésteres metílicos, que fueron analizados más tarde por cromatografía de gases tal como se describió anteriormente. Para el cálculo del grado de descomposición se asumió que las cadenas grasas de tipo ácido palmítico eran resistentes a la degradación. El grado de descomposición térmica (*GDT*), expresado en % en peso, se determinó, tal como describieron Vieitez y col.

[37], mediante la siguiente ecuación:

$$GDT\ (\%) = 100\left[1 - \left(\frac{\sum P_i}{P_{16:0}}\right)_R \left(\frac{P_{16:0}}{\sum P_i}\right)_O\right]$$

donde $\sum P_i$ es la suma del % en peso de todos los ésteres metílicos de ácido graso, $P_{16:0}$ es el % en peso del palmitato de metilo (C16:0) y los subíndices R y O indican que las expresiones entre paréntesis fueron evaluadas considerando la composición del producto de reacción y del aceite original, respectivamente.

Para la aplicación del método Ce 2-66 de la AOCS se pesaron 250 mg de muestra en un erlenmeyer de 50 ml y se añadieron 4 ml de disolución metanólica 0.5 N de NaOH. La mezcla se calentó a reflujo en baño de vapor hasta la disolución total de los glóbulos grasos (unos 5-10 min). A continuación, se añadieron 5 ml de disolución de BF_3 (125 g/l de BF_3 en metanol; disponible comercialmente) y se hirvió durante 2 min más. Luego se añadieron 5 ml de heptano a través del condensador y se hirvió durante 1 min más. Tras retirar la calefacción se añadieron unos 15 ml de disolución acuosa saturada de NaCl, se tapó el erlenmeyer y se agitó vigorosamente, estando aún la disolución tibia, durante unos 15 s. Más tarde, se añadió más disolución saturada de NaCl hasta la flotación de la disolución de heptano. Finalmente, se tomó 1 ml de la disolución de heptano, se le añadió una pequeña cantidad de Na_2SO_4 anhidro y, una vez seca la disolución, se preparó una muestra según indica el procedimiento descrito arriba para la determinación de ésteres metílicos y se inyectó una alícuota de 2 µl en el cromatógrafo de gases.

IV. Resultados y Discusión

Resultados y Discusión

Los principales resultados obtenidos en esta investigación han sido estructurados en base a las respuestas estudiadas: (i) conversión de triglicéridos y rendimiento de biodiésel, (ii) rendimiento de productos intermedios (monoglicéridos y diglicéridos) y (iii) descomposición térmica de las cadenas grasas.

Conversión de triglicéridos y rendimiento de biodiésel

Inicialmente, se estudió la influencia de la temperatura (250-350ºC) y de la relación molar metanol/aceite (20:1-53:1) para un tiempo de reacción de 20 min. En la Figura 1 se muestra la evolución de la conversión de triglicéridos y del rendimiento de biodiésel, observándose que ambas respuestas aumentaban con la relación molar hasta valores de 40:1-45:1 para todas las temperaturas ensayadas, manteniéndose constantes para relaciones molares mayores. La única excepción se observó a 250ºC, temperatura a la que ambas respuestas permanecían prácticamente invariables en todo el intervalo de relaciones molares usadas. Además, independientemente de la relación molar, ambas respuestas aumentaban continuamente con la temperatura de reacción, alcanzándose valores de conversión de triglicéridos y de rendimiento de biodiésel de prácticamente el 100% y de más del 70%, respectivamente, a 350ºC y una relación molar metanol/aceite en torno a 45:1. Estos resultados coinciden con los obtenidos por numerosos autores [14,15,21,39,40], que consiguieron relaciones molares metanol/aceite óptimas comprendidas en el intervalo 40:1-45:1, dependiendo del tipo de aceite empleado y de la temperatura de reacción aplicada.

A continuación, se investigó la influencia del tiempo de reacción (15-90 min) a diferentes temperaturas para una relación molar metanol/aceite de 43:1, que estaba incluida en el rango óptimo indicado anteriormente. La presión alcanzada en el reactor durante los experimentos a 250, 275, 300, 325 y 350ºC fue de 12, 18, 26, 35 y 43 MPa, respectivamente; estos valores eran mayores que la presión crítica del metanol (8.09 MPa). Los principales resultados se presentan en la Figura 2, en la que se aprecia que la conversión de triglicéridos aumentaba continuamente con el tiempo de reacción para temperaturas inferiores a 300ºC. A temperaturas de 300ºC y mayores la conversión llegó a un valor máximo cercano al 98%, que se alcanzaba a tiempos de reacción tanto más cortos cuanto mayor era la temperatura ensayada (56, 33 y 15 min a 300, 325 y 350ºC, respectivamente). En cuanto al rendimiento de biodiésel, éste aumentaba continuamente con el tiempo de reacción para temperaturas de hasta 300ºC, siendo siempre inferior a la conversión de triglicéridos ya que, como se mostrará posteriormente, se detectaron productos intermedios de reacción (monoglicéridos y diglicéridos) en el medio. Por encima de 300ºC el rendimiento de biodiésel pasó por un máximo, que era tanto menor y se alcanzaba a tiempos de reacción tanto más cortos cuanto mayor era la temperatura de reacción; así, el rendimiento máximo logrado a 325ºC (84%) se alcanzó tras 60-75 min de reacción, mientras que a 350ºC se obtuvo tras 20-30 min (70%). La disminución del rendimiento de biodiésel observada para largos tiempos de reacción fue probablemente debida, como se verá más adelante, a la descomposición térmica de los ésteres metílicos poliinsaturados generados.

La mayoría de los autores lograron rendimientos de biodiésel elevados a tiempos de reacción cortos. Así, Saka y Kusdiana [19] obtuvieron un rendimiento del 95% tras unos 4 min de reacción en reactor discontinuo a partir de aceite de colza, mientras que el rendimiento obtenido por Minami y Saka [41] durante la esterificación metílica de ácido oleico en reactor tubular fue del 90% en 30 min. Además, He y col. [21] alcanzaron un rendimiento del 77% tras 25 min a partir de aceite de soja. En nuestro caso, el máximo rendimiento de biodiésel (84%) se obtuvo para tiempos de reacción más largos (60-75 min) y a una temperatura de reacción (325ºC) menor que la indicada por la mayoría de los autores [8,14,17,19,42] (350-360ºC).

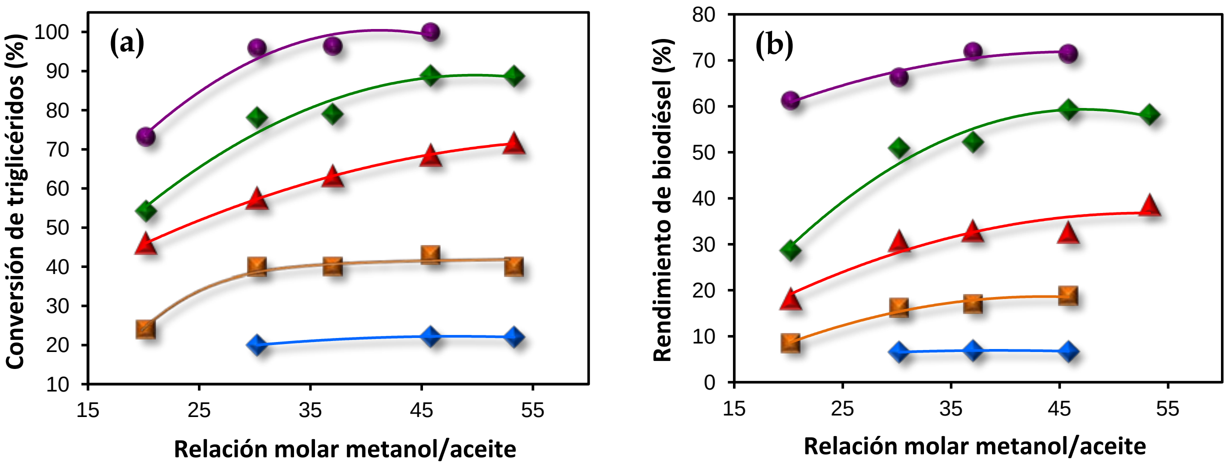

Figura 1. Conversión de triglicéridos (a) y rendimiento de biodiésel (b) en función de la relación molar metanol/aceite para temperaturas de: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC. Tiempo de reacción = 20 min.

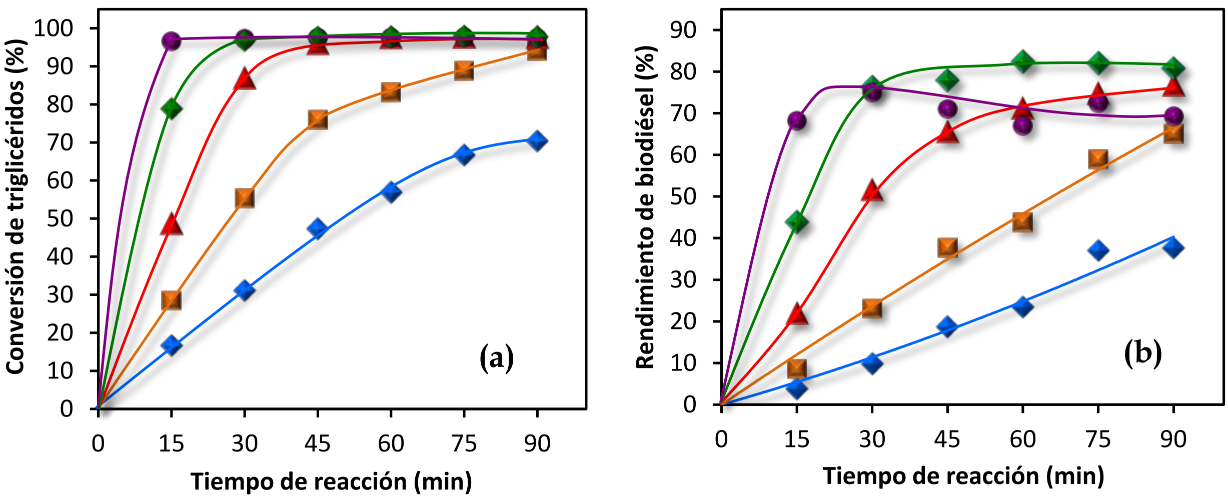

Figura 2. Conversión de triglicéridos (a) y rendimiento de biodiésel (b) en función del tiempo de reacción para temperaturas de: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC. Relación molar metanol/aceite = 43:1.

Rendimiento de monoglicéridos y diglicéridos

Durante la reacción se generaron productos intermedios (monoglicéridos y diglicéridos), cuya evolución a lo largo del tiempo de reacción para temperaturas comprendidas entre 250 y 350ºC se muestra en la Figura 3. En este caso, se usó la relación molar metanol/aceite óptima (43:1). El rendimiento de monoglicéridos aumentó continuamente con el tiempo de reacción para temperaturas de 250 y 275ºC, alcanzándose un valor máximo (37%) a 275ºC. Sin embargo, a temperaturas de 300ºC y superiores el rendimiento de monoglicéridos pasaba por un máximo, que era tanto menor y se alcanzaba a tiempos de reacción tanto más cortos cuanto mayor era la temperatura ensayada. Así, a 300ºC se obtuvo un rendimiento máximo del 34% tras 45 min de reacción, mientras que a 325 y 350ºC el máximo (31 y 27%, respectivamente) se alcanzó tras 26 y 15 min, respectivamente. Vieitez y col. [37] obtuvieron también rendimientos máximos de monoglicéridos en el medio durante la etanólisis supercrítica de aceite de soja refinado, que fueron menores que los conseguidos en este estudio. Tras alcanzarse el máximo, y para tiempos de reacción largos, el rendimiento de monoglicéridos disminuía lentamente, siendo el rendimiento mínimo alcanzado menor cuanto mayor era la temperatura ensayada. Así, a 350ºC se obtuvo un rendimiento mínimo de monoglicéridos del 4.5% tras 90 min de reacción, mientras que a 325ºC el rendimiento mínimo fue del 6.5%, lo que indica que la única manera de reducir el contenido de monoglicéridos en el medio es aumentando la temperatura del proceso.

En cuanto al rendimiento de diglicéridos, éste pasó por un máximo (27-32% a 250-325ºC y 7% a 350ºC) a todas las temperaturas estudiadas. Tras el máximo, el rendimiento de diglicéridos disminuyó hasta alcanzar un valor mínimo que ya se mantuvo prácticamente constante para tiempos más largos. Al igual que en el caso de los monoglicéridos, el rendimiento mínimo de diglicéridos (1.7, 3.3 y 4.9%) era tanto menor cuanto mayor era la temperatura aplicada (350, 325 y 300ºC, respectivamente).

Como era de esperar, independientemente de la temperatura de reacción ensayada, el rendimiento máximo de diglicéridos se alcanzó siempre a tiempos de reacción más cortos que el de monoglicéridos. Este comportamiento es típico de reacciones que se desarrollan en etapas sucesivas, como es el caso de la transesterificación de triglicéridos con metanol, que ocurre en tres etapas consecutivas.

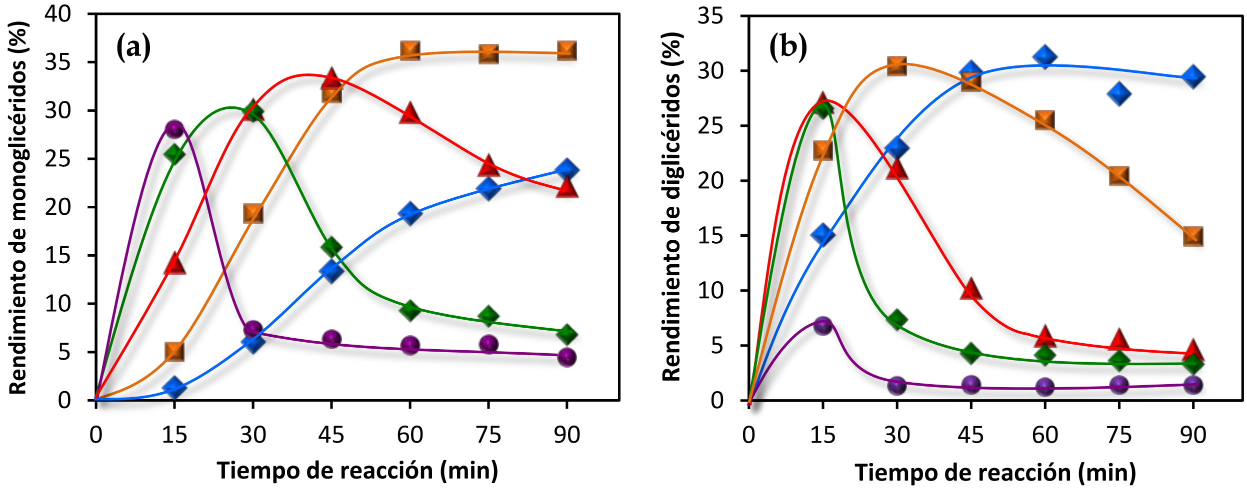

Figura 3. Rendimiento de monoglicéridos (a) y diglicéridos (b) en función del tiempo de reacción para temperaturas de: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC. Relación molar metanol/aceite = 43:1.

Descomposición térmica de las cadenas grasas

Durante el análisis cromatográfico de ciertas muestras de reacción según la norma UNE-EN 14105:2003, que se usa normalmente para la determinación de glicéridos y glicerina libre, se detectó un pico ancho inesperado (Pico 2 en los cromatogramas de la Figura 4). Este nuevo pico, que tenía un tiempo de retención de 20.5-

23.3 min, estaba compuesto por numerosos picos que se superponían y su área aumentaba con la temperatura y el tiempo de reacción (ver la Figura 4), lo que sugería que podía provenir de la descomposición térmica de las cadenas grasas.

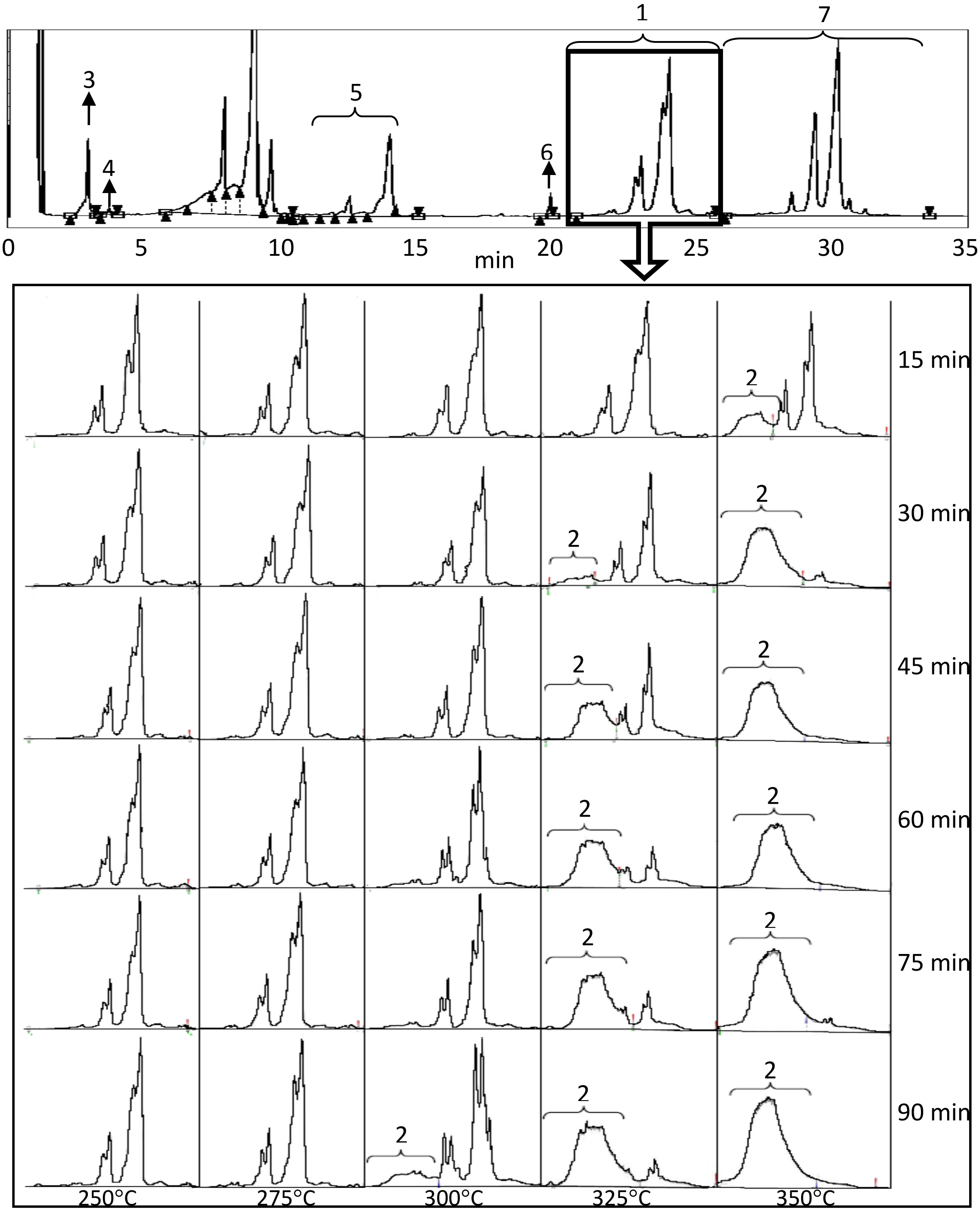

Figura 4. Cromatogramas GC de muestras de reacción obtenidos mediante la aplicación de la norma UNE-EN 14105:2003. Picos cromatográficos: 1 = diglicéridos; 2 = posibles productos de descomposición térmica; 3 = glicerina; 4 = 1,2,4-butanotriol (patrón interno nº 1); 5 = monoglicéridos; 6 = tricaprina (patrón interno nº 2); 7 = triglicéridos. Relación molar metanol/aceite = 43:1.

Para comprobar este hecho se estudió el comportamiento de los principales ésteres metílicos saturados e insaturados (palmitato, oleato, linoleato y linolenato de metilo) generados durante la reacción, comparando su evolución con la del Pico 2 anteriormente indicado.

El palmitato de metilo (C16:0) no descomponía prácticamente en las condiciones de reacción ensayadas, aumentando continuamente su rendimiento con el tiempo de reacción. La única excepción se observó a 350ºC, temperatura a la que se alcanzó una meseta para tiempos largos, a los que el rendimiento disminuyó ligeramente (ver la Figura 5). Además, el mayor rendimiento de palmitato de metilo, logrado a las temperaturas más altas ensayadas (325 y 350ºC), era muy similar al contenido de cadenas grasas de tipo ácido palmítico en el aceite de soja (11.1% mol). En cuanto al oleato de metilo (C18:1), éste tampoco descomponía en las condiciones de reacción aplicadas, aumentando continuamente su rendimiento con el tiempo de reacción hasta alcanzar una meseta para tiempos largos a temperaturas de 300ºC y superiores; además, el rendimiento obtenido en la meseta era mayor conforme aumentaba la temperatura (ver la Figura 6). El mayor rendimiento de oleato de metilo, que se alcanzó a 350ºC, era muy próximo al contenido de cadenas grasas de tipo ácido oleico en el aceite de soja (24.4% mol). Otros autores han obtenido resultados similares en las mismas condiciones de reacción [23,37].

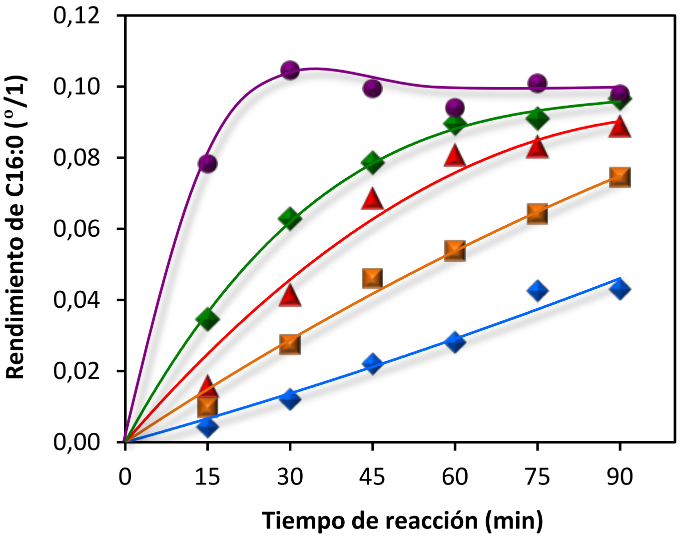

Figura 5. Rendimiento de palmitato de metilo (C16:0) en función del tiempo de reacción para temperaturas de: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC. Relación molar metanol/aceite = 43:1.

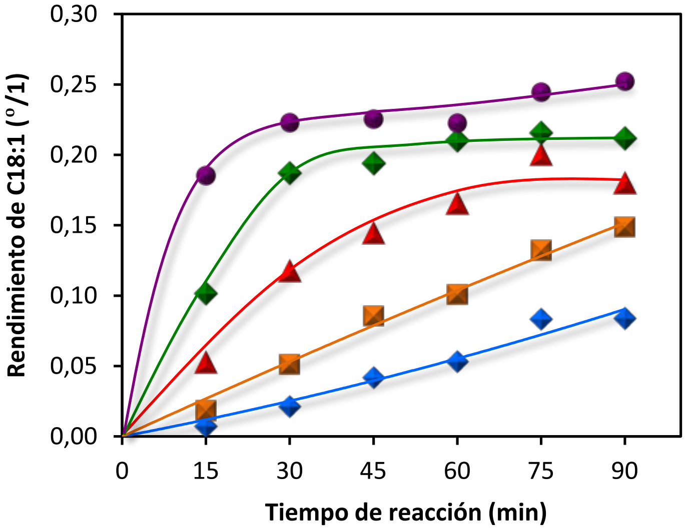

Figura 6. Rendimiento de oleato de metilo (C18:1) en función del tiempo de reacción para temperaturas de: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC. Relación molar metanol/aceite = 43:1.

El linoleato de metilo (C18:2) no descomponía a 250 y 275ºC, aumentando continuamente su rendimiento con el tiempo de reacción (ver la Figura 7). Este comportamiento fue idéntico al observado en la Figura 4, en la que se aprecia claramente que el Pico 2 no era detectado a 250 y 275ºC, incluso para largos tiempos de reacción (90 min). A temperaturas de 300ºC y superiores el rendimiento de linoleato de metilo pasaba por un máximo, que se alcanzaba a tiempos de reacción tanto más cortos cuanto mayor era la temperatura aplicada. Así, el rendimiento máximo se obtuvo tras 75-85 min de reacción a 300ºC, mientras que a 325 y 350ºC se alcanzó tras 50-65 y 5-15 min, respectivamente. El hecho de que se observe un máximo en la evolución del rendimiento de linoleato de metilo parece resultar de dos fenómenos que compiten entre sí: la producción del éster metílico por transesterificación y su degradación por descomposición térmica. Nuevamente se observó un comportamiento idéntico del Pico 2 de la Figura 4; así, este pico empezó a aparecer a 75 min de reacción a 300ºC, coincidiendo con el tiempo en el que el rendimiento de linoleato de metilo empezó a disminuir. Además, el pico aparecía a tiempos de reacción tanto más cortos cuanto mayor era la temperatura ensayada; así, el Pico 2 se observó por primera vez a 30 min (tiempo al que la velocidad de aumento del rendimiento de linoleato de metilo empezó a disminuir [ver la Figura 7]) a 325ºC, mientras que a 350ºC se hizo evidente antes de 15 min, coincidiendo con la disminución del rendimiento de linoleato de metilo. Más allá del rendimiento máximo obtenido a cada temperatura (300, 325 y 350ºC), el rendimiento de linoleato de metilo disminuía (tanto más lentamente cuanto más baja era la temperatura) debido probablemente a la descomposición térmica de este compuesto, que fue menos intensa conforme disminuía la temperatura aplicada. El rendimiento máximo alcanzado a 300, 325 y 350ºC fue siempre menor que el contenido de cadenas grasas de tipo ácido linoleico en el aceite de soja (53.1% mol) y era tanto más pequeño conforme aumentaba la temperatura, indicando de nuevo la existencia de reacciones de descomposición térmica, que eran más intensas cuanto mayor era la temperatura aplicada. He y col. [21] también observaron la descomposición térmica del linoleato de metilo por encima de 300ºC durante la metanólisis supercrítica de aceite de soja.

En el caso del linolenato de metilo (C18:3), éste se comportaba de manera similar al linoleato de metilo, aumentando su rendimiento de manera continua a lo largo del tiempo de reacción para temperaturas menores de 300ºC. A temperaturas de 300ºC y superiores el rendimiento pasaba por un máximo (ver la Figura 8), que era siempre más pequeño que el contenido de cadenas grasas de tipo ácido linolénico en el aceite de soja (7.2% mol), indicando claramente que este éster metílico descomponía térmicamente en estas condiciones de reacción. La degradación térmica del linolenato de metilo también fue observada por otros autores en condiciones de reacción similares [23,37], de manera que los productos de descomposición térmica de este compuesto también podían contribuir a la formación del Pico 2 de los cromatogramas indicados en la Figura 4, si bien en una extensión mucho menor que el linoleato de metilo ya que el contenido de cadenas grasas de tipo ácido linolénico en el aceite de soja es mucho más pequeño.

Por lo tanto, se puede concluir que el Pico 2, detectado cromatográficamente tras la aplicación de la norma UNE-EN 14105:2003, estaba compuesto prácticamente en su totalidad por productos de descomposición térmica de los ésteres metílicos insaturados que contenían dos o más dobles enlaces ya que la desaparición (como resultado de la descomposición térmica) de los principales ésteres metílicos poliinsaturados generados durante la reacción supercrítica coincidía exactamente con la formación de este nuevo pico.

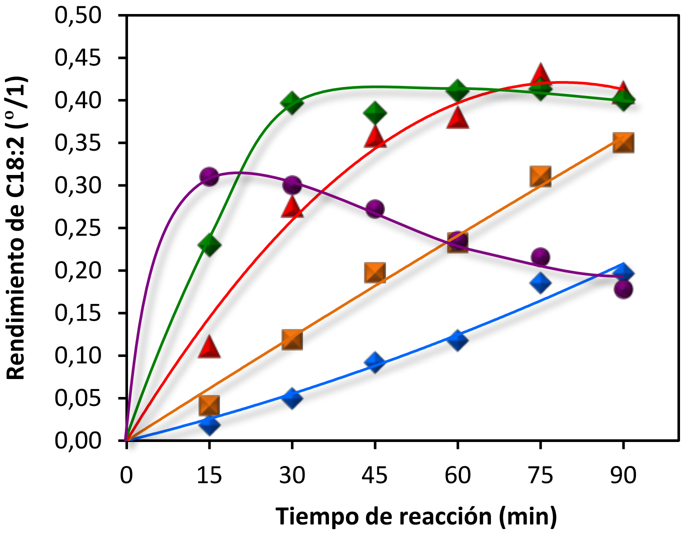

Figura 7. Rendimiento de linoleato de metilo (C18:2) en función del tiempo de reacción para temperaturas de: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC. Relación molar metanol/aceite = 43:1.

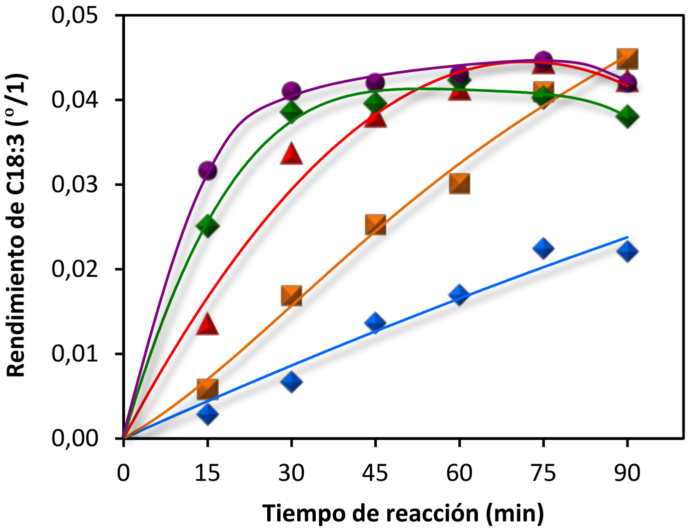

Figura 8. Rendimiento de linolenato de metilo (C18:3) en función del tiempo de reacción para temperaturas de: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC. Relación molar metanol/aceite = 43:1.

Con el fin de confirmar la existencia de reacciones indeseables de degradación térmica de las cadenas de ácido graso y cuantificar el grado de descomposición de las mismas se usó el método descrito por Vieitez y col. [37]. Este método se aplicó a muestras obtenidas en diferentes condiciones de reacción (temperatura, 250-350ºC; tiempo de reacción, 15-90 min; relación molar metanol/aceite, desde 13:1 a 53:1). La presión en el reactor fue de 10-12 MPa a 250ºC, 16-18 MPa a 275ºC, 23-26 MPa a 300ºC, 30-35 MPa a 325ºC y 36-41 MPa a 350ºC, dependiendo su valor, dentro de los rangos de presión indicados, de la relación molar usada. Además, dentro de estos rangos el efecto de la presión sobre la reacción supercrítica fue pequeño [21].

Independientemente del tiempo de reacción y de la relación molar, no se observó descomposición térmica a 250 y 275ºC (ver la Figura 9). La descomposición comenzó a ser evidente a 300ºC para todas las relaciones molares ensayadas a partir de unos 60 min, mientras que a 325 y 350ºC se observó prácticamente desde el inicio de la reacción (15 min), aumentando el grado de descomposición térmica con la temperatura y el tiempo de reacción. Así, el mayor grado de descomposición se alcanzó a 350ºC tras 90 min de reacción para todas las relaciones molares ensayadas, obteniéndose valores máximos de 40.1, 36.3, 35.5, 28.2 y 27.2% en estas condiciones para relaciones molares metanol/aceite de 13:1, 23:1, 33:1, 43:1 y 53:1, respectivamente. Vieitez y col. [37,43] obtuvieron resultados similares durante la etanólisis supercrítica de aceite de soja en reactor tubular.

El grado de descomposición térmica no variaba prácticamente con la relación molar a 300ºC tras 90 min de reacción, ni a 325 y 350ºC tras 15 min, condiciones en las que se obtuvieron valores de 4.0–5.0, 3.6–4.9 and 9.8–11.9%, respectivamente. Sin embargo, a 325 y 350ºC el grado de descomposición decrecía con la relación molar para tiempos de reacción de 45 min y más largos. Además, la disminución de la descomposición térmica con la relación molar metanol/aceite a temperaturas mayores de 300ºC y tiempos de reacción más largos de 45 min coincidía con el aumento del rendimiento de los ésteres metílicos poliinsaturados, lo que parece indicar que la relación molar metanol/aceite favorece la síntesis de biodiésel ya que tiene un cierto efecto protector contra la descomposición térmica de éstos ésteres metílicos.

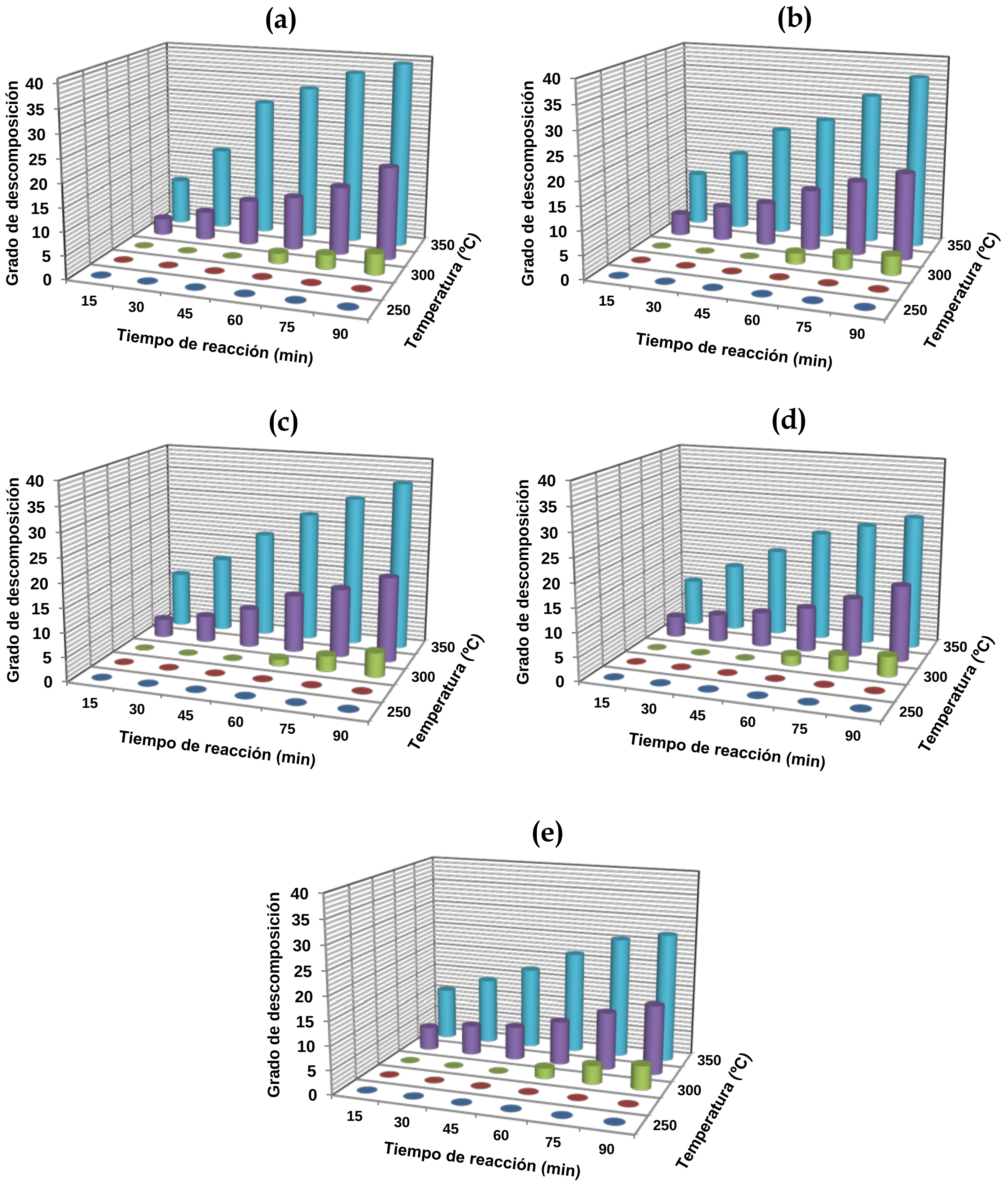

Figura 9. Grado de descomposición térmica (% peso) de las cadenas grasas en función de la temperatura y del tiempo de reacción para relaciones molares metanol/aceite de: (a) 13:1, (b) 23:1, (c) 33:1, (d) 43:1, y (e) 53:1.

Se ha llevado a cabo un análisis de regresión lineal simple para examinar la relación que existe entre el grado de descomposición térmica de las cadenas grasas y la relación de áreas entre el nuevo pico cromatográfico detectado (el Pico 2 de los cromatogramas de la Figura 4, que correspondía a los productos de descomposición térmica) y el pico de la tricaprina (patrón interno utilizado por la norma UNE-EN 14105:2003). Se encontró cierta dificultad para determinar con precisión el área del Pico 2 cuando el grado de descomposición era bajo (entre 3 y 6%) ya que este pico se superponía con algunos de los picos correspondientes a los diglicéridos; sin embargo, en la mayoría de los casos en los que las condiciones de reacción provocaban mayores grados de descomposición térmica, apenas se detectaron diglicéridos en el medio ya que éstos desaparecían rápidamente con la severidad de la reacción.

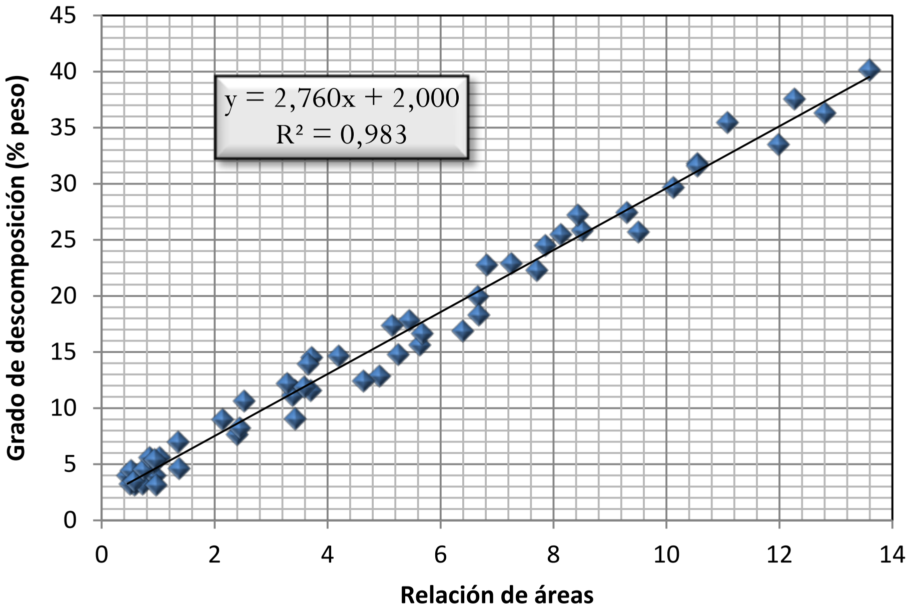

Figura 10. Relación entre el grado de descomposición térmica y la relación de áreas entre el pico correspondiente a los productos de descomposición térmica y el de la tricaprina (patrón interno).

En la Figura 10 se representa el grado de descomposición térmica de las cadenas grasas frente a la relación de áreas entre los dos picos cromatográficos (indicados anteriormente) para 55 experimentos llevados a cabo en diferentes condiciones de reacción (300-350ºC, 15-90 min y relaciones molares de 13:1 a 53:1). Como se puede apreciar, los puntos tendían hacia una línea recta. Por lo tanto, el ajuste de los datos de la Figura 10 a un modelo de regresión lineal simple dio lugar a una recta de regresión por mínimos cuadrados ($Y = 2.0002 + 2.7604X$, donde Y representa el grado de descomposición térmica, expresado en % en peso, y X representa la relación de áreas entre los dos picos cromatográficos) con un coeficiente de correlación r de 0.9911, un coeficiente de determinación r^2 de 0.9831, un coeficiente r^2 ajustado de 0.9827 y una desviación típica de 1.3838. El buen ajuste de los datos a este sencillo modelo de regresión lineal permite predecir adecuadamente el grado de descomposición térmica de las cadenas grasas en función de la relación de áreas entre el pico correspondiente a los productos de descomposición térmica (el nuevo pico detectado) y el pico de la tricaprina. Por lo tanto, la norma UNE-EN 14105:2003, que se usa normalmente para la determinación de glicéridos y glicerina libre, puede ser también empleada directamente para cuantificar el grado de descomposición térmica de las cadenas grasas durante la síntesis de biodiésel con metanol supercrítico a partir de aceite de soja refinado.

V. Conclusiones

Conclusiones

I. Se ha diseñado un reactor discontinuo cilíndrico de 84 ml de capacidad que fue construido en acero inoxidable A310 y probado a temperaturas y presiones de hasta 450ºC y 75 MPa, respectivamente.

II. Se han puesto a punto métodos analíticos para la determinación de: (i) monoglicéridos, diglicéridos y triglicéridos por cromatografía de permeación en gel (GPC), (ii) ésteres metílicos por cromatografía de gases (GC/FID) según la norma UNE-EN 14103:2003, (iii) glicerina libre, monoglicéridos, diglicéridos y triglicéridos por cromatografía de gases (GC/FID) según la norma UNE-EN 14105:2003, y (iv) el grado de descomposición térmica de las cadenas de ácido graso por cromatografía de gases (GC/FID) tras la aplicación del método oficial Ce 2-66 de la AOCS.

III. Se ha detectado un nuevo pico cromatográfico (con un tiempo de retención de 20.5–23.3 min y formado por numerosos picos superpuestos) durante el análisis de las muestras de reacción según la norma UNE-EN 14105:2003, que está compuesto fundamentalmente por los productos de descomposición térmica de los ésteres metílicos poliinsaturados.

IV. Se ha demostrado que el área de este nuevo pico cromatográfico detectado puede ser usada para cuantificar el grado de descomposición térmica de las cadenas grasas.

V. Se ha obtenido un modelo de regresión lineal simple [$Y = 2.0002 + 2.7604X$, donde Y representa el grado de descomposición térmica y X representa la relación de áreas entre el pico correspondiente a los productos de descomposición térmica y el pico de la tricaprina (patrón interno usado por la norma UNE-EN 14105:2003)] por mínimos cuadrados que permite predecir adecuadamente el grado de descomposición térmica de las cadenas grasas en función de la relación de áreas entre estos dos picos cromatográficos.

VI. Se ha encontrado que las mejores condiciones de reacción (relación molar metanol/aceite de 43:1, 325ºC/35 MPa y 60 min), que conducen al mayor rendimiento de biodiésel (84%), dan lugar a cierto grado de descomposición térmica de las cadenas grasas (7.9%).

VII. Se ha observado que la síntesis de biodiésel con metanol supercrítico en reactor discontinuo debe realizarse a temperaturas por debajo de 300ºC para evitar la descomposición térmica de las cadenas de ácido graso, obteniéndose en estas condiciones un rendimiento máximo de biodiésel del 72% tras 60 min de reacción.

VIII. Se ha evidenciado que para todas las relaciones molares ensayadas (desde 13:1 a 53:1) empiezan a aparecer reacciones indeseables de descomposición térmica de las cadenas grasas insaturadas a partir de 300ºC, siendo éstas más intensas conforme aumenta la temperatura y el tiempo de reacción. La degradación térmica de éstas comenzó tras 60 min de reacción a 300ºC, mientras que a 325 y 350ºC lo hizo prácticamente desde los primeros momentos de la reacción (15 min).

IX. Se ha encontrado que las cadenas grasas saturadas empiezan a descomponer a partir de 350ºC.

X. Se ha observado que la relación molar metanol/aceite no solo favorece la formación de los ésteres metílicos saturados e insaturados, sino que además tiene un cierto efecto protector contra la descomposición térmica de los ésteres metílicos poliinsaturados.

XI. Se ha evidenciado en general que el rendimiento conjunto de monoglicéridos y diglicéridos pasa por un máximo de entre el 50 y el 65% a lo largo del proceso, dependiendo de las condiciones de reacción.

XII. Se ha obtenido que el rendimiento máximo de diglicéridos se alcanza siempre a tiempos de reacción más cortos que el de monoglicéridos, lo que corresponde a un comportamiento típico de una reacción de tres etapas en serie.

XIII. Se ha encontrado que para conversiones de triglicéridos superiores al 90% se produce una disminución drástica del contenido de monoglicéridos y diglicéridos en el medio, aumentando de manera importante el rendimiento de biodiésel. Sin embargo, independientemente de las condiciones de reacción, siempre permanece en el medio una pequeña cantidad de estos productos intermedios.

XIV. Se ha obtenido siempre un rendimiento de biodiésel inferior a la conversión de triglicéridos ya que, por un lado, parte de éstos se transforman en monoglicéridos y diglicéridos sin convertirse íntegramente en ésteres metílicos y, por otro lado, una porción de los ésteres metílicos generados descompone térmicamente.

VI. Bibliografía

Bibliografía

[1] S. Gryglewicz, Rapeseed oil methyl esters preparation using heterogeneous catalysts, Bioresource Technology 70 (1999) 249- 253.

[2] S. Furuta, H. Matsuhashi, K. Arata, Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure, Catalysis Communications 5 (2004) 721-723.

[3] C.J. Shieh, H.F. Liao, C.C. Lee, Optimization of lipase-catalyzed biodiesel by response surface methodology, Bioresource Technology 88 (2003) 103-106.

[4] D.Y.C. Leung, X. Wu, M.K.H. Leung, A review on biodiesel production using catalyzed transesterification, Applied Energy 87 (2010) 1083-1095.

[5] B. Freedman, E.H. Pryde, T.L. Mounts, Variables affecting the yields of fatty esters from transesterified vegetable oils, Journal of American Oil Chemists' Society 61 (1984) 1638-1643.

[6] F. Ma, L.D. Clements, M.A. Hanna, The effects of catalyst, free fatty acids, and water on transesterification of beef tallow, Transactions of the ASAE 41 (1998) 1261-1264.

[7] Y. Warabi, D. Kusdiana, S. Saka, Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols, Bioresource Technology 91 (2004) 283-287.

[8] D. Kusdiana, S. Saka, Effects of water on biodiesel fuel production by supercritical methanol treatment, Bioresource Technology 91 (2004) 289-295.

[9] B. Freedman, R.O. Butterfield, E.H. Pryde, Transesterification kinetics of soybean oil, Journal of American Oil Chemists' Society 63 (1986) 1375-1380.

[10] A.W. Schwab, M.O. Bagby, B. Freedman, Preparation and properties of diesel fuels from vegetable oils, Fuel 66 (1987) 1372-1378.

[11] F. Ma, M.A. Hanna, Biodiesel production: a review, Bioresource Technology 70 (1999) 1-15.

[12] R. Sawangkeaw, K. Bunyakiat, S. Ngamprasertsith, A review of laboratory scale research on lipid conversion to biodiesel with supercritical methanol (2001

2009), Journal of Supercritical Fluids 55 (2010) 1-13.

[13] M.M. Gui, K.T. Lee, S. Bhatia, Supercritical ethanol technology for the production of biodiesel: process optimization studies, Journal of Supercritical Fluids 49 (2009) 286-292.

[14] E.S. Song, J.W. Lim, H.S. Lee, Y.W. Lee, Transesterification of RBD palm oil using supercritical methanol, Journal of Supercritical Fluids 44 (2008) 356-363.

[15] A. Demirbas, Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics, Energy Conversion and Management 47 (2006) 2271-2282.

[16] P. Valle, A. Velez, P. Hegel, G. Mabe, E.A. Brignole, Biodiesel production using supercritical alcohols with a non-edible vegetable oil in a batch reactor, Journal of Supercritical Fluids 54 (2010) 61-70.

[17] G. Madras, C. Kolluru, R. Kumar, Synthesis of biodiesel in supercritical fluids, Fuel 83 (2004) 2029-2033.

[18] T. Pinnarat, P.E. Savage, Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions, Industrial and Engineering Chemistry Research 47 (2008) 6801-6808.

[19] S. Saka, D. Kusdiana, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel 80 (2001) 225-231.

[20] D. Kusdiana, S. Saka, Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol, J. Chemical Engineering of Japan 34 (2001) 383-387.

[21] H. He, T. Wang, S. Zhu, Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process, Fuel 86 (2007) 442-447.

[22] H.Y. Shin, S.M. Lim, S.Y. Bae, S.C. Oh, Thermal decomposition and stability of fatty acid methyl esters in supercritical methanol, J. Analytical and Applied Pyrolysis 92 (2011) 332-338.

[23] H. Imahara, E. Minami, S. Hari, S. Saka, Thermal stability of biodiesel in supercritical methanol, Fuel 87 (2008) 1-6.

[24] M.M. Conceiçao, V.J. Fernandes, A.S. Araújo, M.F. Farias, I.M.G. Santos, A.G.

Souza, Thermal and oxidative degradation of castor oil biodiesel, Energy and Fuels 21 (2007) 1522-1527.

[25] I.S. Patrikios, P.C. Patsalis, Monounsaturated fatty acid oligomerization is responsible for the agglutination activity of heated virgin olive oil, Food Research International 36 (2003) 985-990.

[26] I. Vieitez, C. Silva, I. Alckmin, F. Castilhos, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Stability of ethyl esters from soybean oil exposed to high temperatures in supercritical ethanol, J. Supercritical Fluids 56 (2011) 265-270.

[27] V.F. Marulanda, G. Anitescu, L.L. Tavlarides, Biodiesel fuels through a continuous flow process of chicken fat supercritical transesterification, Energy and Fuels 24 (2010) 253-260.

[28] N. Aimaretti, D.L. Manuale, V.M. Mazzieri, C.R. Vera, J.C. Yori, Batch study of glycerol decomposition in one-stage supercritical production of biodiesel, Energy and Fuels 23 (2009) 1076-1080.

[29] S. Lee, D. Posarac, N. Ellis, An experimental investigation of biodiesel synthesis from waste canola oil using supercritical methanol, Fuel 91 (2012) 229-237.

[30] W. Iijima, Y. Kobayashi, K. Takekura, K. Taniwaki, The nonglycerol process of biodiesel fuel treated in supercritical methanol, in: Presented at the 2004 ASAE/CSAE Annual International Meeting, Ottawa, ON, Canada, 2004, Paper No. 046073.

[31] G. Anitescu, A. Deshpande, L.L. Tavlarides, Integrated technology for supercritical biodiesel production and power cogeneration, Energy and Fuels 22 (2008) 1391-1399.

[32] V.F. Marulanda, G. Anitescu, L.L. Tavlarides, Investigations on supercritical transesterification of chicken fat for biodiesel production from lowcost lipid feedstocks, J. Supercritical Fluids 54 (2010) 53-60.

[33] R. Sawangkeaw, S. Teeravitud, K. Bunyakiat, S. Ngamprasertsith, Biofuel production from palm oil with supercritical alcohols: effects of the alcohol to oil molar ratios on the biofuel chemical composition and properties, Bioresource Technology 102 (2011) 10704-10710.

[34] H. Noureddini, W.R. Dailey, B.A. Hunt, Production of ethers of glycerol from crude glycerol–the byproduct of biodiesel production, Chemical and Biomolecular Engineering Research and Publications, Papers in Biomaterials, University of Nebraska (1998) 1-14.

[35] M. Ikura, Conversion of glycerol to naphtha-range oxygenates, US Patent application number 20100016641 (2010).

[36] P. Pepiot-Desjardins, H. Pitsch, R. Malhotra, S. Kirby, A. Boehman, Structural group analysis for soot reduction tendency of oxygenated fuels, Combustion and Flame 154 (2008) 191-205.

[37] I. Vieitez, C. Silva, I. Alkimim, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Effect of temperature on the continuous synthesis of soybean esters under supercritical ethanol, Energy & Fuels 23 (2009) 558-563.

[38] G. Arzamendi, E. Arguiñarena, I. Campo, L.M. Gandía, Monitoring of biodiesel production: Simultaneous analysis of the transesterification products using size-exclusion chromatography, Chemical Engineering Journal 122 (2006) 31-40.

[39] D. Kusdiana, S. Saka, Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, Fuel 80 (2001) 693-698.

[40] L. Wang, H. He, Z. Xie, J. Yang, S. Zhu, Transesterification of the crude oil of rapeseed with NaOH in supercritical and subcritical methanol, Fuel Processing Technology 88 (2007) 477-481.

[41] E. Minami, S. Saka, Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process, Fuel 85 (2006) 2479-2483.

[42] K.T. Tan, K.T. Lee, A.R. Mohamed, Production of FAME by palm oil transesterification via supercritical methanol technology, Biomass and Bioenergy 33 (2009) 1096-1099.

[43] I. Vieitez, C. Silva, I. Alckmin, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Continuous catalyst-free methanolysis and ethanolysis of soybean oil under supercritical alcohol/water mixtures, Renewable Energy 35 (2010) 1976–1981.

VII. Publicaciones

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Supercritical Biodiesel Production from Raw Soybean Oil

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ABSTRACT

This paper describes the supercritical methanol transesterification of raw soybean oil for biodiesel production in a batch stirred tank reactor without catalyst and looks at the main variables affecting the yield of biodiesel: the methanol-to-oil molar ratio and reaction temperature. Experiments were carried out for 20 min in the temperature range 250-350°C at methanol-to-oil molar ratios of between 20:1 and 53:1. The reactions were monitored by gel permeation chromatography (GPC) to determine the content of monoglycerides, diglycerides and triglycerides, and by gas chromatography (GC/FID) to analyse the individual methyl esters and to calculate the yield of biodiesel. The reaction conditions that led to good yields of biodiesel (72%) were a temperature of 350°C and a methanol-to-oil molar ratio of 45. There was no undesirable thermal decomposition of the fatty acid chains in these conditions. Due to the risk of thermal cracking above 350ºC, reaction times need to be lengthened to complete the transesterification of monoglycerides and diglycerides remaining in the medium and so provide greater yields of biodiesel.

Keywords: Biodiesel, Supercritical methanol, Soybean oil, Transesterification conditions.

1. INTRODUCTION

Biodiesel has emerged as an alternative fuel and gained wide acceptance because of some advantages it has over petroleum derived diesel: lower environmental impact [1], higher lubricity, higher cetane number and lower flash point. Biodiesel is made from the triglycerides that exist in biomass, such as animal fats, plant oils (*e.g.*, corn, palm, rapeseed and soybean oils) and algae. Waste cooking oils and animal fats are especially attractive feedstocks because they are inexpensive and provide a waste-to-energy opportunity.

Biodiesel can be produced by catalyzed or uncatalyzed transesterification. The former process is currently used in commercial biodiesel production, while the latter method, which typically involves supercritical conditions, was developed to facilitate processing of lower quality, and hence lower cost, feedstocks. However, biodiesel synthesis using supercritical methanol has a drawback: the high cost of the necessary apparatus which uses high temperature and pressure, and which are therefore unsuitable for large scale industrial production. This has led to many researchers to look for ways to decrease the severity of the reaction conditions. For example, co-solvents, such as carbon dioxide [2] and propane [3], and heterogeneous catalysts, such as calcium oxide [4], added into the reaction mixture can decrease the operating temperature, the working pressure and the amount of alcohol. In the supercritical method, the acid value and water content do not have a negative effect on the reaction, and may even provide an impetus to the reaction under certain conditions [5]. Furthermore, purification of the reaction products is simpler than in the catalyzed process and non-polluting effluents are generated.

In the research described, biodiesel production from raw soybean oil with supercritical methanol in a batch stirred tank reactor was investigated without the use of catalysts. Experiments were carried out for 20 min, and the influence of the reaction temperature (250-350°C) and the methanol-to-oil molar ratio (20:1-53:1) was studied. In the near future, once the optimal reaction conditions have been established, a study using heterogeneous catalysts (prepared jointly by the University of the Basque Country and the

Public University of Navarra, Spain) will be carried out in a search for milder reaction conditions, which will lower production costs even more.

2. EXPERIMENTAL SETUP

The reaction was carried out for 20 min in a batch stirred tank reactor (a stainless steel cylindrical autoclave of 83 ml capacity) to investigate the influence of the reaction temperature (250-350ºC) and the methanol-to-oil molar ratio (20:1-53:1). The reactor was introduced pneumatically by a mechanical arm into a smelted salt bath which permits the reaction mixture to reach the desired temperature in less than 9 min. In all the experiments, the reaction time started when the reactor was immersed in the salt bath. The reactor was continuously shaken orbitally (70 rpm), and, after removal from the salt bath, introduced in a water bath to stop the reaction. The product obtained was evaporated in rotavapor to remove the methanol and stored in refrigerator before analysis.

The reaction was monitored by gel permeation chromatography (GPC) to determine the content of monoglycerides, diglycerides and triglycerides, and by gas chromatography (GC/FID) to analyse the individual methyl esters and to calculate the yield of biodiesel according to the UNE-EN 14103:2003 norm. Two apparatus used were: (1) a LC-Module I Waters liquid cromatograph coupled to a 2414 Waters refractive index detector and fitted with two Styragel GPC columns (HR0.5 and HR1, 7.8 x 300 mm and 5 ìm particle size) connected in series. The analysis were carried out in isochratic conditions using tetrahydrofuran as eluent at 0.9 ml/min; (2) a 3900 Varian gas chromatograph equipped with a CP 8400 Varian autosampler, coupled to a FID detector and fitted with a CP-Wax 52-CB capillary column (30 m x 0.32 mm, 0.25 ìm film). Helium was used as carrier gas at a flow rate of 1 ml/min with a split ratio of 1:50. The oven temperature was always 210ºC. The injector and detector temperature was 250°C.

3. RESULTS AND DISCUSSION

The main results obtained during the transesterification of soybean oil with supercritical methanol are shown in Tables 1 and 2, where the influence of the methanol-to-oil molar ratio and temperature on the reaction can be observed. The yield of biodiesel was calculated in two ways: (1) taking into account all the methyl esters (peaks) detected in the GC chromatogram (total biodiesel), and (2) taking into account only the identified methyl esters (known biodiesel); in both cases, the yield was calculated as a percentage of the quantity of methyl esters that can theoretically be obtained from the fatty acid composition of the oil.

To avoid any influence of the methanol-to-oil molar ratio on the working pressure, we initially studied the influence of the volume of methanol used to fill the reactor (84 ml capacity) on the pressure reached inside the reactor at different temperatures (see Figure 1). As expected, it was observed that, regardless of the filling volume of the reactor, the higher the temperature, the greater the pressure inside the reactor. Moreover, the higher the filling volume of the reactor, the greater the dependence between temperature and pressure. The introduction of volumes above 60 ml of methanol led to excessively high pressures, even at the lowest temperature tested (250°C), which could endanger the safe operation of the reactor. With a filling volume of 60 ml, a pressure of 225 bar was reached at 250ºC, whereas at 350ºC the pressure was 400 bar. Because this pressure range (225-400 bar) is the most commonly studied by authors [6, 7], a filling volume of 60 ml was chosen for all the experiments. On the other hand, when the reactor was filled only with oil, the amount introduced does not cause a significant increase in pressure, and values lower than 20 bar are reached, regardless of the temperature applied. As shown in Figure 2, with a filling volume of 60 ml (methanol + oil), the pressure reached inside the reactor for different temperatures and methanol-to-oil molar ratios was little influenced by the molar ratio, whatever the temperatura applied, the only exception being the 20.2 molar ratio.

Table 1. Conversion of the oil and yield of monoglycerides, diglycerides and biodiesel during transesterification of soybean oil with supercritical methanol.

M/O	T (ºC)	P (bar)	CO (%)	YD*	YM*	YTB (%)	YKB (%)
20.20	275	83	24.00	130.30	21.72	8.51	1.57
20.20	300	107	45.99	239.75	45.18	18.11	16.17
20.20	325	128	54.30	168.08	105.16	28.66	27.36
20.20	353	283	73.23	48.34	72.48	61.27	56.10
30.20	257	112	20.01	115.32	12.51	6.58	5.53
30.20	280	200	40.03	193.72	41.90	16.19	14.01
30.20	305	256	57.47	254.12	84.65	30.77	28.47
30.20	330	325	78.17	126.74	110.95	51.00	46.50
30.20	350	390	95.90	45.42	82.27	66.32	61.37
37.00	278	192	40.05	191.90	36.16	17.03	14.96
37.00	304	280	63.23	267.03	86.41	32.93	30.41
37.00	330	360	79.00	167.46	124.09	52.27	48.84
37.00	352	445	96.47	43.55	83.85	71.95	66.34
45.80	257	141	22.20	128.47	25.66	6.92	6.07
45.80	284	235	43.04	189.79	41.16	18.81	18.18
45.80	308	290	68.47	246.56	93.06	32.58	30.06
45.80	330	377	88.89	148.99	123.77	59.30	54.94
45.80	354	454	100.00	48.16	87.43	71.49	73.43
53.30	259	145	22.02	128.20	27.87	6.76	5.20
53.30	280	220	40.03	201.17	42.51	13.76	11.93
53.30	306	298	71.60	266.80	110.41	38.55	35.42
53.30	325	374	88.76	183.08	132.74	58.23	54.47

M/O = methanol-to-oil molar ratio; T = reaction temperature; P = working pressure; CO = conversion of oil; YD = yield of diglycerides; YM = yield of monoglycerides; YTB = yield of total biodiesel (g of methyl esters detected/g of theoretical methyl esters); YKB = yield of known biodiesel (g of methyl esters identified/g of theoretical methyl esters); *expressed in mg/g of initial triglycerides.

The conversion of oil and the yield of biodiesel, monoglycerides and diglycerides were studied during reaction. The conversion of oil and the yield of biodiesel, both total and known, as a function of reaction temperature are represented in Figures 3, 4 and 5, respectively, for different methanol-to-oil molar ratios. The differences between the yield of total and known biodiesel are quite small, indicating that practically all the methyl esters detected were identified and that, therefore, no methyl esters other than those indicated in the method were generated. It was observed that both the conversion of oil and the yield of biodiesel increased with temperature, a conversion close to 100% at 350°C being reached, regardless of the methanol-to-oil molar ratio used, with the exception of the molar ratio of 20.2, which led to a conversion of around 70%. At the same temperature (350ºC) we obtained the highest yield of total biodiesel (close to 70% for molar ratios above 30), which was significantly lower than the conversion of oil. The fact that the yield of biodiesel was always lower than the conversion of oil at all temperatures indicates that part of the triglycerides were not converted to methyl esters, but probably to intermediate products such as monoglycerides and diglycerides. It was also noted that both the conversion of oil and the yield of biodiesel increased slightly with the methanol-to-oil molar ratio, whatever the temperature. The pressure remaining in the reactor after

Table 2. Yield of the individual methyl esters obtained during transesterification of soybean oil with supercritical methanol (mg/g of initial triglycerides).

M/O	T (ºC)	RC 14:0	RC 16:0	RC 16:1	RC 18:0	RC 18:1	RC 18:2	RC 18:3	RC 20:0	RC 20:1
20.20	275	0.00	9.34	0.00	2.25	4.08	0.00	0.00	0.00	0.00
20.20	300	0.00	21.36	0.00	7.16	39.38	91.02	2.75	0.00	0.00
20.20	325	0.20	34.29	0.00	12.02	63.26	144.83	17.12	0.63	0.12
20.20	353	0.43	78.39	0.92	32.74	163.76	273.86	5.63	2.63	1.43
30.20	257	0.00	7.69	0.00	2.43	12.95	29.70	2.53	0.00	0.00
30.20	280	0.00	18.41	0.00	6.32	33.80	79.55	1.99	0.00	0.00
30.20	305	0.22	37.64	0.30	13.40	68.84	157.12	5.93	0.61	0.61
30.20	330	0.36	68.51	0.00	21.80	127.44	239.90	6.98	0.00	0.00
30.20	350	0.46	93.53	0.00	30.93	180.96	290.12	17.69	0.00	0.00
37.00	278	0.00	20.36	0.00	6.31	35.97	84.72	2.23	0.00	0.00
37.00	304	0.23	40.19	0.00	14.37	72.09	170.17	7.04	0.00	0.00
37.00	330	0.37	63.79	0.00	22.65	119.49	267.94	14.20	0.00	0.00
37.00	352	0.57	96.44	1.08	34.21	180.66	334.37	9.13	2.88	2.73
45.80	257	0.00	8.59	0.00	2.48	14.35	35.26	0.00	0.00	0.00
45.80	284	0.00	23.37	0.00	7.44	42.90	100.71	7.35	0.00	0.00
45.80	308	0.26	40.48	0.00	13.37	71.26	168.85	6.41	0.00	0.00
45.80	330	0.41	66.63	0.00	26.30	138.30	301.24	11.08	1.90	1.30
45.80	354	0.57	105.10	0.00	34.34	200.13	376.85	17.28	0.00	0.00
53.30	259	0.00	7.25	0.00	0.82	13.07	30.85	0.00	0.00	0.00
53.30	280	0.00	14.87	0.00	3.96	29.12	70.17	1.17	0.00	0.00
53.30	306	0.31	47.01	0.00	15.05	85.86	198.48	7.51	0.00	0.00
53.30	325	0.47	69.50	0.00	22.51	132.32	300.75	18.96	0.12	0.11

M/O = Methanol-to-oil molar ratio; T = reaction temperature; RC14:0, RC16:0, RC16:1, RC18:0, RC18:1, RC18:2, RC18:3, RC20:0, RC20:1 y RC22:1 = yield of methyl ester of fatty acid chain C14:0, C16:0, C16:1, C18:0, C18:1, C18:2, C18:3, C20:0, C20:1 and C22:1, respectively.

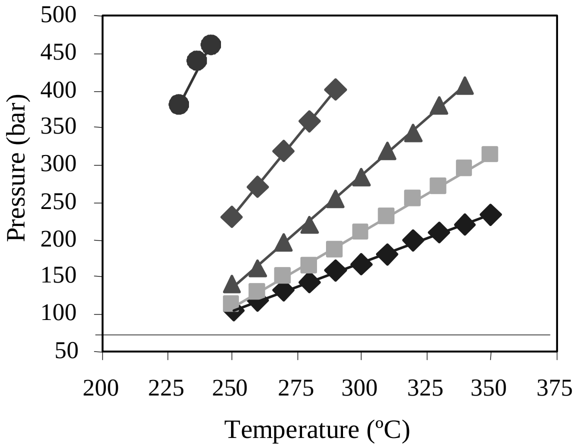

Figure 1. Pressure generated in the reactor as a function of temperature for filling volumes of methanol of: ◆, 30 ml; ■, 40 ml; ▲, 50 ml; ◆, 60 ml; ●, 70 ml.

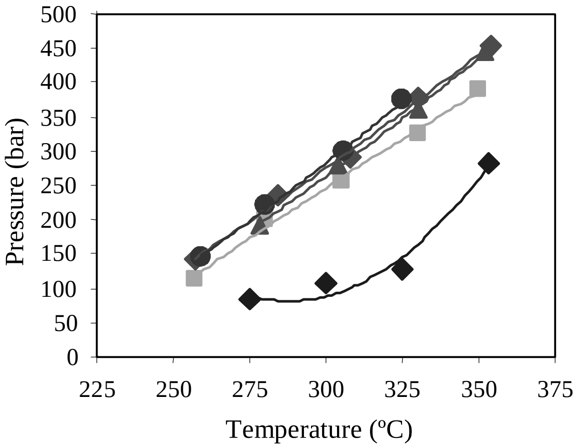

Figure 2. Pressure generated in the reactor as a function of reaction temperature for methanol-to-oil molar ratios of: ◆, 20.2; ■, 30.2; ▲, 37; ◆, 45.8; ●, 53.3 (filling volume of the reactor = 60 ml, reaction time = 20 min).

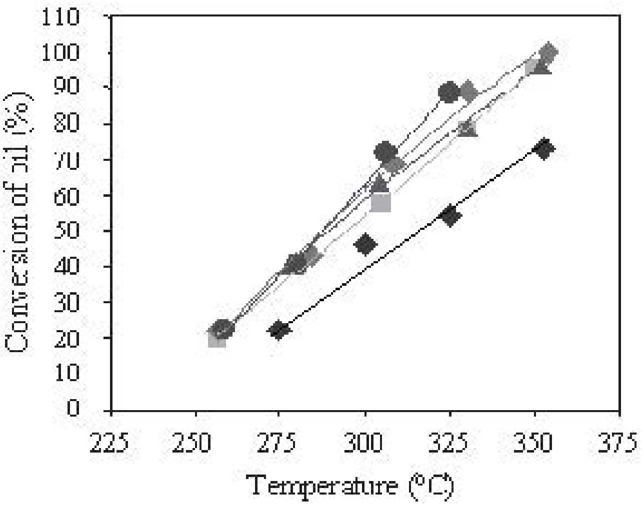

Figure 3. Conversion of oil as a function of reaction temperature for methanol-to-oil molar ratios of: ◆, 20.2; ■, 30.2; ▲, 37; ◆, 45.8; ●, 53.3 (reaction time = 20 min).

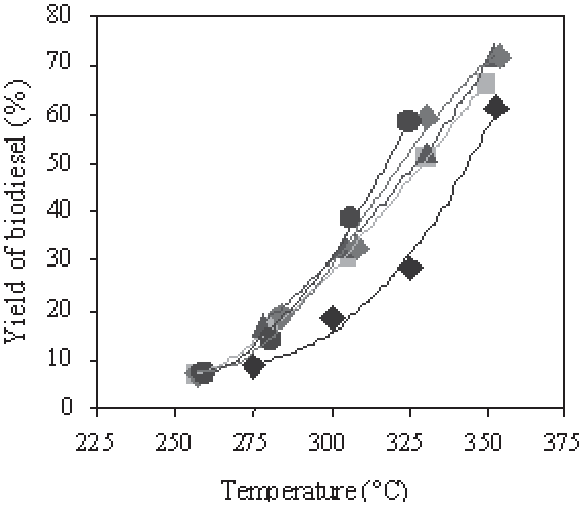

Figure 4. Yield of total biodiesel as a function of reaction temperature for methanol-to-oil molar ratios of: ◆, 20.2; ■, 30.2; ▲, 37; ◆, 45.8; ●, 53.3 (reaction time= 20 min).

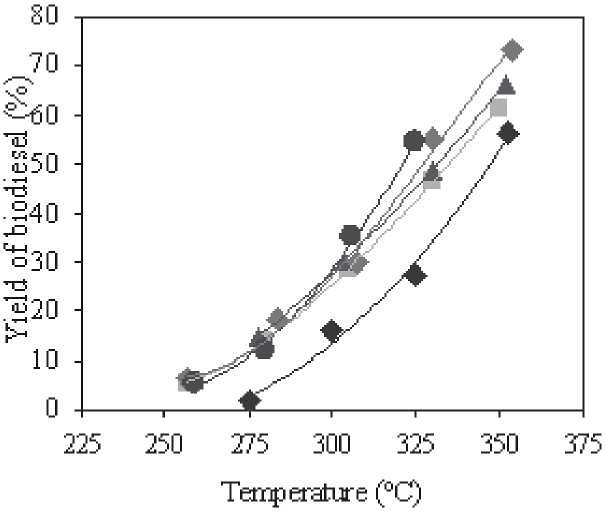

Figure 5. Yield of known biodiesel as a function of reaction temperature for methanol-to-oil molar ratios of: ◆, 20.2; ■, 30.2; ▲, 37; ◆, 45.8; ●, 5 3.3 (reaction time = 20 min).

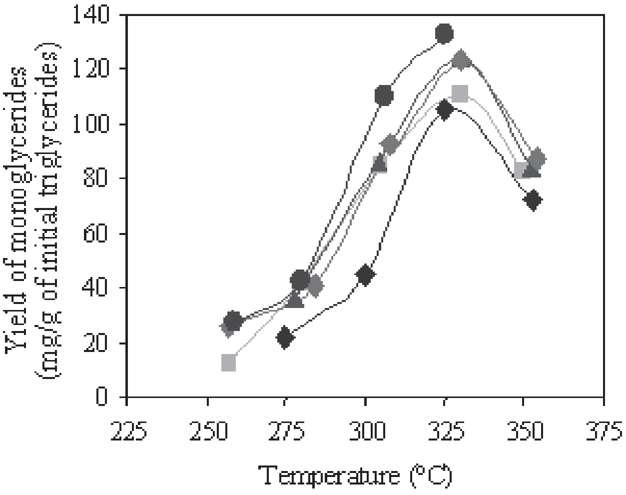

Figure 6. Yield of monoglycerides as a function of reaction temperature for methanol-to-oil molar ratios of: ◆, 20.2; ■, 30.2; ▲, 37; ◆, 45.8; ●, 53.3 (reaction time = 20 min).

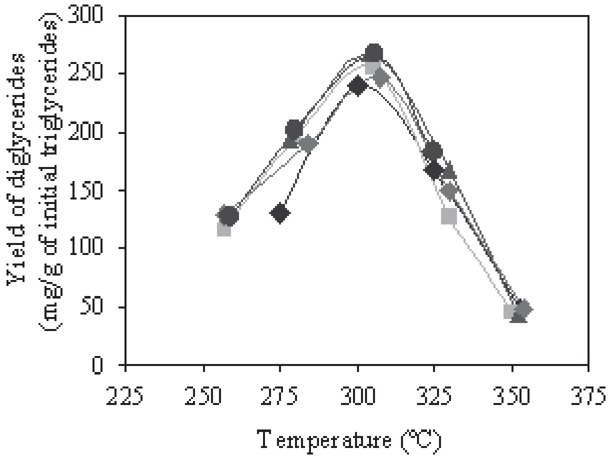

Figure 7. Yield of diglycerides as a function of reaction temperature for methanol-to-oil molar ratios of: ◆, 20.2; ■, 30.2; ▲, 37; ◆, 45.8; ●, 53.3 (reaction time = 20 min).

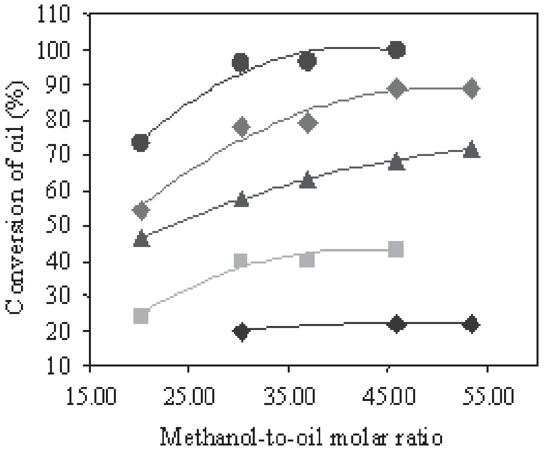

Figure 8. Conversion of oil as a function of methanol-to-oil molar ratio for reaction temperatures of: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC (reaction time = 20 min).

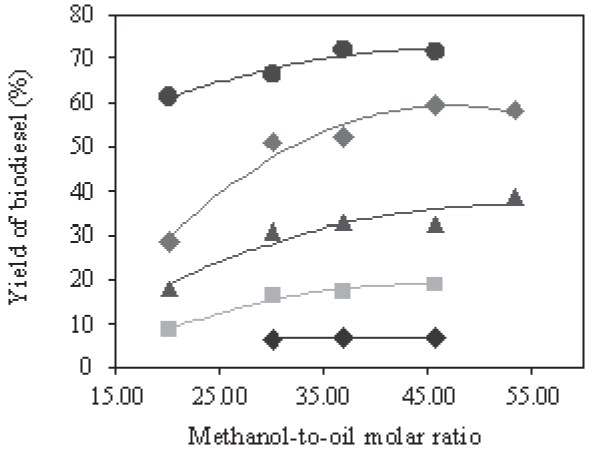

Figure 9. Yield of total biodiesel as a function of methanol-to-oil molar ratio for reaction temperatures of: ◆, 250ºC; ■, 275ºC; ▲, 300ºC; ◆, 325ºC; ●, 350ºC (reaction time = 20 min).

the reaction was always atmospheric, suggesting the absence of thermal cracking reactions of the fatty acid chains, which would normally lead to the formation of methane and carbon dioxide. Since temperatures above 350°C may cause these undesirable reactions, it is not recommended to work at temperatures above 400ºC [7]. Therefore, it can be concluded that the best reaction conditions to carry out the transesterification of soybean oil with supercritical methanol were a temperature of 350ºC for 20 min and a methanol-to-oil molar ratio of 45.8. These results are consistent with those obtained by several authors [7-11] who indicated an optimal temperature within the range 300-350°C and a molar ratio of 40-45.

The yield of monoglycerides (see Figure 6) passed through a maximum at about 325ºC for all the methanol-to-oil molar ratios studied. This maximum (between 105 and 132 mg/g of initial triglycerides) increases with the molar ratio applied. As shown in Figure 7, the behavior of diglycerides was similar, reaching a maximum of 267 mg/g of initial triglycerides at about 300°C for a methanol-to-oil molar ratio of 53.3; in this case, the maximum was little influenced by the molar ratio. The trends observed suggest that diglycerides would disappear at about 360ºC, whereas the yield of monoglycerides would become zero at about 400ºC. The disappearance of monoglycerides and diglycerides would lead to higher yields of biodiesel, which would be close to 100% if there were no thermal decomposition reactions of the fatty acid chains.

Table 3. Mass balance in the reactor for supercritical methanol transesterification of soybean oil.

M/O	T (°C)	ME*	MG*	DG*	TG*	Gly*	MeOH*	TG+ MeOH*	ME+MG+ DG+ Gly*	Error (%)
20.2	275	85.0	21.7	130.3	241.0	25.3	26.4	267.4	262.3	1.9
20.2	300	180.9	45.2	239.7	452.0	47.4	49.5	501.5	513.2	-2.3
20.2	325	286.2	105.2	168.1	543.0	57.0	59.4	602.5	616.4	-2.3
20.2	353	612.0	72.5	48.3	732.3	76.8	80.2	812.5	809.6	0.4
30.2	257	65.7	12.5	115.3	198.0	20.8	21.7	219.7	214.3	2.5
30.2	280	161.7	41.9	193.7	402.0	42.2	44.0	446.0	439.4	1.5
30.2	305	307.3	84.7	254.1	574.7	60.3	62.9	637.6	706.4	-10.8
30.2	330	509.3	110.9	126.7	781.7	82.0	85.6	867.3	829.0	4.4
30.2	350	662.4	82.3	45.4	959.0	100.6	105.0	1064.0	890.7	16.3
37.0	278	170.1	36.2	191.9	405.0	42.5	44.3	449.3	440.6	1.9
37.0	304	328.9	86.4	267.0	632.3	66.3	69.2	701.5	748.7	-6.7
37.0	330	522.0	124.1	167.5	790.0	82.9	86.5	876.5	896.4	-2.3
37.0	352	718.6	83.8	43.6	964.7	101.2	105.6	1070.3	947.2	11.5
45.8	257	69.1	25.7	128.5	221.0	23.2	24.2	245.2	246.4	-0.5
45.8	284	187.9	41.2	189.8	430.0	45.1	47.1	477.1	463.9	2.8
45.8	308	325.4	93.1	246.6	684.7	71.8	75.0	759.7	736.9	3.0
45.8	330	592.3	123.8	149.0	888.9	93.2	97.3	986.2	958.3	2.8
45.8	354	714.0	87.4	48.2	1000.0	104.9	109.5	1109.5	954.5	14.0
53.3	259	67.6	27.9	128.2	222.0	23.3	24.3	246.3	246.9	-0.2
53.3	280	137.5	42.5	201.2	398.0	41.7	43.6	441.6	422.9	4.2
53.3	306	385.0	110.4	266.8	716.0	75.1	78.4	794.4	837.3	-5.4
53.3	325	581.6	132.7	183.1	887.6	93.1	97.2	984.8	990.5	-0.6

M/O = methanol-to-oil molar ratio; T = reaction temperature; ME = methyl esters generated; MG = monoglycerides generated; DG = diglycerides generated; TG = triglycerides converted; Gly = theoretical glycerine generated; MeOH = theoretical methanol reacted; *expressed in mg/g of initial triglycerides; Error = [(TG+MeOH)-(ME+MG+DG+Gly)]·100/(TG+MeOH).

As shown in table 2, the individual yield of the main methyl esters obtained increases with reaction temperature and only slightly with the methanol-to-oil molar ratio, although this increase was very small for molar ratios above 30. As expected, the highest yields obtained were those of methyl palmitate, methyl oleate and methyl linoleate because soybean oil has a high content of these kinds of fatty acid chain.

According to some authors [7, 12], thermal decomposition and dehydrogenation (undesirable reactions) of unsaturated fatty acid chains (particularly those of linoleic and linolenic acid type) occurs at temperatures between 300 and 350°C, with a consequent loss of biodiesel yield. In our study, the yield of the main unsaturated fatty acid methyl esters (methyl oleate, methyl linoleate and methyl linolenate) did not decrease in the temperature range tested (250-350ºC) (see Table 2), indicating that undesirable decomposition reactions of fatty acid chains were not produced in the experimental conditions applied.

To clearly observe the influence of the methanol-to-oil molar ratio on the conversion of oil and the yield of total biodiesel, Figures 8 and 9 represent these two responses versus the molar ratio for temperatures of 250, 275, 300, 325 and 350°C. As can be seen, both the conversion of oil and the yield of biodiesel increase with the molar ratio up to molar ratios of 40-45, above which these two responses leveled off for all temperatures tested, the only exception being at 250°C, at which the responses remained practically constant over the entire range of molar ratios tested. These results agree with those obtained by other authors [7-11], who obtained optimum molar ratios in the range 40-45, depending on the type of oil used and the reaction temperature applied.

Table 3 shows the mass balance in the reactor. The balance was made taking into account that in each experiment, the sum of the amount of triglycerides converted and the theoretical amount of methanol reacted (calculated from the amount of methyl esters generated) must be equal to the sum of the generated amounts of methyl esters, monoglycerides and diglycerides plus the theoretical amount of glycerol generated. As can be seen, the results indicate that the mass balance in the reactor was correctly accomplished (error lower than 5% in most cases, and not exceeding 16% in any case), indicating that no undesirable side or thermal decomposition reactions were produced.

4. CONCLUSIONS

Based on the results obtained, it can be concluded that the transesterification conditions of soybean oil with supercritical methanol that lead to good yields of biodiesel (72%), without producing undesirable thermal cracking reactions of fatty acid chains, are a temperature of 350°C applied for 20 min and a methanol-to-oil molar ratio of 45. Because the application of temperatures above 350ºC can lead to the thermal decomposition of fatty acid chains, greater yields of biodiesel could be achieved by applying longer reaction times to complete the transesterification of monoglycerides and diglycerides remaining in the medium.

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REFERENCES

1. Kiwjaroun C, Tubtimdee C and Piumsomboon P. LCA studies comparing biodiesel synthesized by conventional and supercritical methanol methods. Journal of Cleaner Production **2009**; 17: 143-153.
2. Han H, Cao W and Zhang J. Preparation of biodiesel from soybean oil using supercritical methanol and CO_2 as co-solvent. Process Biochemistry **2005**; 40: 3148-3151.
3. Cao W, Han H and Zhang J. Preparation of biodiesel from soybean oil using supercritical methanol and co-solvent. Fuel **2005**; 84: 347-351.
4. Demirbas A. Biodiesel from sunflower oil in supercritical methanol with calcium oxide. Energy Conversion and Management **2007**; 48: 937-941.
5. Kusdiana D and Saka S. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresource Technology **2004**; 91: 289-295.
6. Saka S and Kusdiana D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel **2001**; 80: 225-231.
7. Kusdiana D and Saka S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel **2001**; 80: 693-698.
8. Song ES, Lim JW, Lee HS and Lee YW. Transesterification of RBD palm oil using supercritical methanol. Journal of Supercritical Fluids **2008**; 44: 356-363.
9. Demirbas A. Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics. Energy Conversion and Management **2006**; 47: 2271-2282.
10. Wang L, He H, Xie Z, Yang J and Zhu S. Transesterification of the crude oil of rapeseed with NaOH in supercritical and subcritical methanol. Fuel Processing Technology **2007**; 88: 477-481.
11. He H, Wang T and Zhu S. Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. Fuel **2007**; 86: 442-447.
12. Imahara H, Minami E, Hari S and Saka S. Thermal stability of biodiesel in supercritical methanol. Fuel **2008**; 87: 1-6.

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Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol

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New evidence on the thermal decomposition of fatty acid methyl esters during biodiesel synthesis in supercritical conditions is presented. Thermal decomposition products were detected chromatographically, by applying the UNE-EN 14105:2003 standard, as a broad single peak during the determination of glycerides in the reaction samples. These degradation products could be quantified chromatographically by the above standard because the area of the peak was proportional to the disappearance of the polyunsaturated fatty acid methyl esters, which contain two or more double bonds (methyl linoleate and linolenate), generated during biodiesel synthesis from soybean oil. In the experimental conditions tested, thermal decomposition reactions of these unsaturated fatty acid methyl esters began to appear at 300 °C/26 MPa, and were more intense as the temperature rose. For its part, the main saturated fatty acid methyl ester (methyl palmitate) generated during the reaction was hardly decomposed at all in the experimental conditions tested and only began to disappear at 350 °C/43 MPa.

1. Introduction

Biodiesel has emerged as an alternative fuel and gained wide acceptance because of the advantages it has over petroleum derived diesel: these include lower environmental impact [1], higher lubricity, higher cetane number and lower flash point. Unlike petroleum derived diesel, biodiesel is biodegradable and non-toxic, and it significantly reduces toxic and other emissions when burned as a fuel. Biodiesel is made from the triglycerides that exist in biomass, such as animal fats, plant oils (e.g., corn, palm, rapeseed and soybean oils) and algae. Current worldwide production of vegetable oil and animal fat is not enough to replace the use of liquid fossil fuel (maximum replacement percentage: ~20–25%) [2].

The transesterification reaction to produce biodiesel can be alkali-catalyzed [3], acid-catalyzed [4] or enzyme-catalyzed [5]. An excess of methanol is necessary to shift the reaction to the right side in order to achieve a high yield of fatty acid methyl esters (FAMEs) (biodiesel). To improve production by the commonly used homogeneous phase alkali-catalyzed method, refined vegetable oils with a free fatty acid (FFA) content lower than 0.5% (acid value lower than 1) should be used [6]; the presence of FFAs may cause ester saponification and catalyst consumption, reducing the catalyst efficiency. Moreover, the water content of the oil has a greater negative effect than FFAs and should be kept below 0.06% [7] because it hinders complete conversion of the oil/fat.

Most industries use pre-treatment steps to reduce the FFA and water content of the feedstock. FFAs are usually removed by esterification with methanol in the presence of sulfuric acid. However, this pre-treatment step not only causes the production process to be less efficient [8], but also increase costs.

The main drawback of biodiesel is that it is more expensive than petroleum diesel fuel. Most of the cost is related to acquiring the triglyceride feedstock. Therefore, inexpensive feedstocks, such as waste cooking oils and animal fats, are especially attractive for their waste-to-energy capacity. The main problem of using waste cooking oils for biodiesel synthesis is its high water (up to 3 wt%) and FFA (more than 6 wt%) content, which hinders their use for conventional alcali-catalyzed production.

Transesterification in supercritical reaction conditions has been used for catalyst-free biodiesel synthesis. In such conditions, the mixture between methanol and oil becomes a single homogeneous phase, which accelerates the reaction because there is no interphase mass transfer to limit the reaction rate. In addition, the non-catalytic supercritical process has environmental advantages because there is no waste generated as a result of catalyst treatment and separation from the final product. Furthermore, this non-catalytic method requires no pretreatment of the feedstock because impurities in the feed do not strongly affect the reaction. When water and FFAs are present in the feed, three types of reaction (transesterification, triglyceride hydrolysis and alkyl esterification of fatty acids) occur simultaneously . Alkyl esterification is faster than transesterification and ensures that all FFAs in the feed, whether present originally or as products of hydrolysis, are completely transformed into fatty acid alkyl esters [9]. Further-

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more, separation of the biodiesel product and glycerol byproduct is simple because the products are not miscible at ambient temperature and there is no catalyst in the mixture to be removed. In addition, in this uncatalyzed process, there is no soap formation, as might occur in the alkali-catalyzed process as a result of FFAs reacting with catalyst.

Though supercritical conditions possess some advantages, there are also disadvantages. The high alcohol to oil ratio used in experiments (>40:1), if used commercially, would create difficulties in separating the biodiesel from the excess methanol for its recovery and reuse. An additional drawback of employing supercritical conditions is the high temperature and pressure used (300–350 °C/20–50 MPa for a product yield of 95% in only 4–15 min [10–16]), which require more energy and/or a process well engineered for energy recovery, and perhaps higher capital costs for the reactor. They are, therefore, unsuitable for large scale industrial production.

This has led to many researchers to look for ways to decrease the severity of the reaction conditions. For example, co-solvents, such as carbon dioxide [17] and propane [18], and heterogeneous catalysts, such as calcium oxide [19], added into the reaction mixture, can decrease the operating temperature, the working pressure and the amount of alcohol added.

In the severe conditions necessary for supercritical biodiesel production, the thermal stability of biodiesel is a major concern [11,20–22]. As is well known, polyunsaturated fatty acids are reactive and thus vulnerable to denaturations, for example through oxidation.

In the research described here, the evolution of the main unsaturated and saturated FAMEs generated during uncatalyzed supercritical biodiesel synthesis with methanol from refined soybean oil in a batch stirred tank reactor was investigated and qualitatively compared with that of the decomposition products detected by gas chromatography during the determination of the glyceride content in the reaction samples. The experimental conditions investigated to determine the thermal stability of various FAMEs were a temperature in the range of 250–350 °C, which corresponded to pressures between 12 and 43 MPa, and a reaction time of between 15 and 90 min, always maintaining a methanol-to-oil molar ratio of 43:1.

2. Materials and methods

2.1. Materials

A commercial refined soybean oil supplied by Lesieur Cristal (Roche Noires, Casablanca, Maroc), whose fatty acid composition is shown in Table 1, was used for this study. Anhydrous methanol was supplied by Panreac Química, S.A.U. (Castellar del Vallès, Barcelona, Spain), while methyl heptadecanoate, 1,2,4-butanetriol, 1,2,3-tricaproylglycerol (tricaprin), monoolein, diolein, triolein and glycerol were supplied by Sigma–Aldrich (Tres Cantos, Madrid, Spain) and used as standards.

Table 1
Fatty acids composition of commercial refined soybean oil (mol%).

Palmitic acid (C16:0)	11.1
Stearic acid (C18:0)	3.7
Oleic acid (C18:1)	24.4
Linoleic acid (C18:2)	53.1
Linolenic acid (C18:3)	7.2
Other acids	0.5
Total	100.0

2.2. Selection of the supercritical reaction conditions

The set of experimental conditions used in this research was selected according to the critical temperature and pressure of methanol (239.45 °C and 80.9 bar), the solvent used as a reagent for the synthesis of biodiesel. Methanol is currently the most widely used solvent for industrial scale biodiesel production.

The variables which most strongly influence the transesterification reaction in biodiesel synthesis in supercritical conditions are the reaction temperature, the methanol-to-oil molar ratio and the reaction time. Other variables that influence the reaction were the operating pressure (directly related to the reaction temperature and the filling volume of the batch reactor) and the stirring rate of the reaction medium [23].

The most commonly used temperatures and methanol-to-oil molar ratios are in the ranges 240–400 °C and 6–60, respectively. At temperatures above the critical, the methanol–vegetable oil mixture is homogenized, so that the reaction develops much faster and may only take a few minutes. As regards the reaction time, this is usually set at between 5 and 50 min [24–26], depending on the reaction temperature applied. The best reaction conditions in a batch reactor which lead to a high yield of biodiesel (close to 100%) are similar regardless of the type of oil used. Thus, the reaction is completed in 4–25 min at 300–350 °C and applying a methanol-to-oil molar ratio of 40–45 [13,14,24,25].

In the present study, the reaction temperature was in the range 250–350 °C. The lower limit of this range (250 °C) is slightly higher than the critical temperature of methanol (239.45 °C), and is therefore in the supercritical domain, while the upper limit (350 °C) was established because above this temperature the yield of biodiesel usually decreases [13,22]. For its part, the reaction time used in this study was between 15 and 90 min, the longer time than normal being chosen to determine its influence on the side reactions of thermal decomposition of the fatty acid methyl esters generated during the reaction. In this research, a methanol-to-oil molar ratio of 43 was fixed for all the experiments since this is regarded as the best value by most authors [11,13,22].

2.3. Working method

The reaction was carried out in a batch stirred tank reactor (a stainless steel cylindrical autoclave of 83 ml capacity) to investigate the influence of the reaction temperature (250–350 °C) and reaction time (15–90 min). In each of the experiments, the reactor was loaded with 50 g of methanol–soybean oil mixture and introduced pneumatically by a mechanical arm into a smelted salt bath which permits the reaction mixture to reach the desired temperature in about 10 min. In all the experiments, the reaction time started when the reactor was immersed in the salt bath. The reactor was continuously shaken orbitally (70 rpm) during the reaction, and, after removal from the salt bath, introduced in a water bath to stop the reaction. The product obtained was evaporated by rotavapor to remove the remaining methanol and stored in a refrigerator before analysis.

2.4. Analytical methods

The reaction was monitored by gas chromatography (GC/FID) to determine the content of glycerides (monoglycerides, diglycerides and triglycerides) and glycerine, and to analyse the individual methyl esters. The apparatus used was a 3900 Varian gas chromatograph equipped with a CP 8400 Varian autosampler and coupled to a FID detector.

2.4.1. Analysis of glycerides and glycerine

The analysis of monoglycerides, diglycerides, triglycerides and glycerine was performed according to the standard UNE-EN

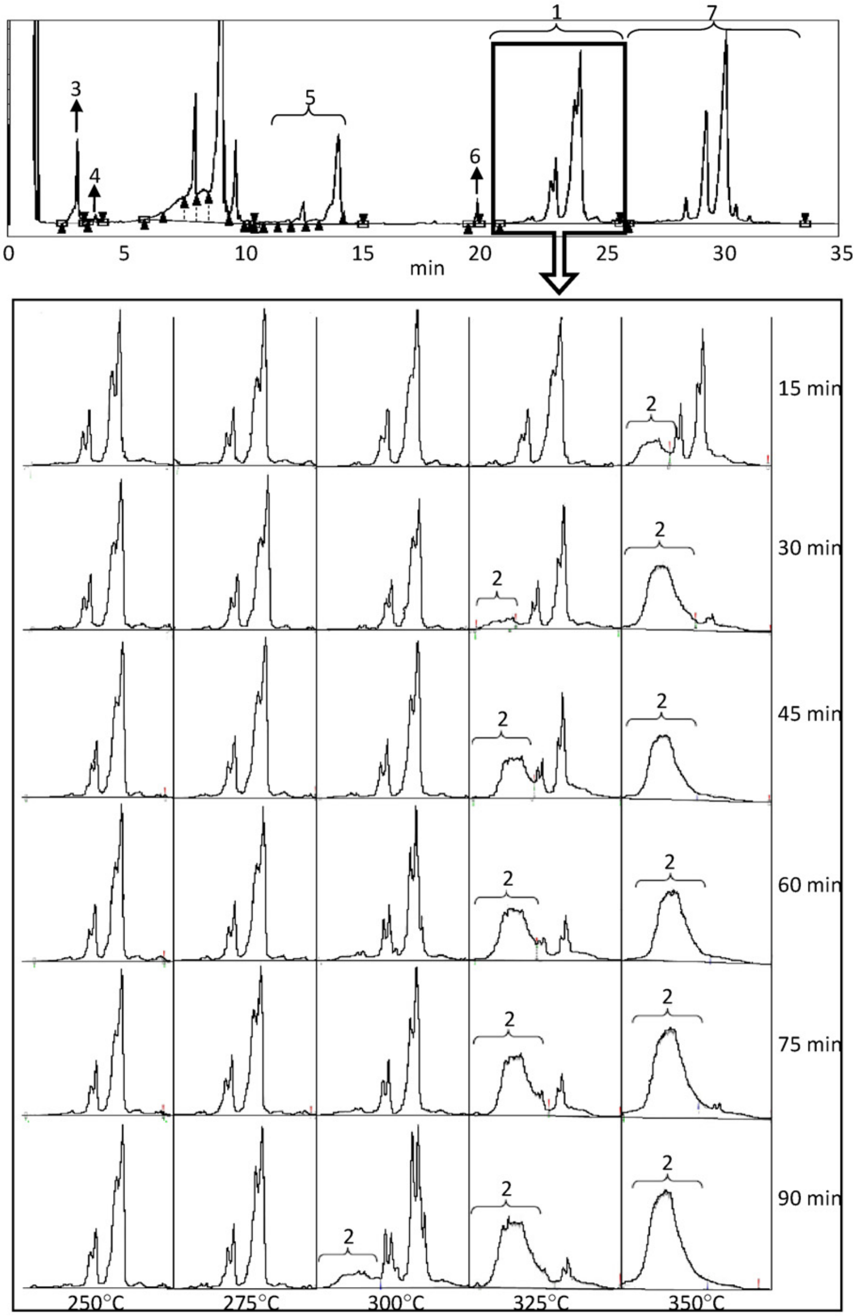

Fig. 1. GC chromatograms of reaction samples obtained by applying the standard UNE-EN 14105:2003. Chromatographic peaks: 1 = diglycerides; 2 = possible thermal decomposition products; 3 = glycerine; 4 = 1,2,4-butanetriol (internal standard no. 1); 5 = monoglycerides; 6 = glyceryl tridecanoate (internal standard no. 2); 7 = triglycerides.

14105:2003. The principle of the method is based on the transformation of glycerides and glycerine into their respective silylated derivatives, which are more volatile. The silylation is carried out using N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) and in the presence of pyridine. The method requires two internal standard solutions: (a) no. 1, obtained by dissolving 50 mg of 1,2,4-butanetriol in 50 ml of pyridine in a volumetric flask; and (b) no. 2, obtained by dissolving 80 mg of 1,2,3-tricaproylglycerol (tricaprin) in 10 ml of pyridine in a volumetric flask.

100 mg of sample was weighed into a vial of 10 ml, and then 80 μl of standard solution no. 1, 100 μl of standard solution no. 2 and 100 μl of MTSFA were added, avoiding contact with moisture. Subsequently, the vial was closed tightly, shaken vigorously and allowed to stand for 15 min at room temperature. Finally, 8 ml of heptane was added and an aliquot of 2 μl was injected into the gas chromatograph.

The chromatograph was fitted with a FactorFour VF-5ht capillary column (10 m × 0.32 mm, 0.1 μm film). Helium was used as carrier gas at a flow rate of 1 ml/min with a split ratio of 1:70. The temperature ramp of the oven was: 1 min at 50 °C, 15 °C/min to 180 °C, 7 °C/min to 230 °C, 10 °C/min to 370 °C and 5 min at 370 °C. The temperature of detector was 380 °C and that of the injector 280 °C.

2.4.2. *Analysis of methyl esters*

To determine the individual methyl esters the standard UNE-EN 14103:2003 was applied. For this, 250 mg of sample was dissolved in 5 ml of standard solution (prepared in a volumetric flask by dissolving 500 mg of methyl heptadecanoate in 50 ml of heptane) in a 10 ml vial. Then, the vial was closed with teflon cap and shaken vigorously. Finally, 2 μl of the solution obtained was injected into the gas chromatograph.

The apparatus was fitted with a CP-Wax 52-CB capillary column (30 m × 0.32 mm, 0.25 μm film). Helium was used as carrier gas at a flow rate of 1 ml/min with a split ratio of 1:50. The temperature of the oven was always 210 °C and that of the injector and detector 250 °C.

3. Results and discussion

The pressure reached in the reactor during experiments at 250, 275, 300, 325 and 350 °C was 12, 18, 26, 35 and 43 MPa, respectively, regardless of the reaction time. These values were higher than the critical pressure of methanol (8.09 MPa), and practically the same as those reported by other authors for similar temperatures [20].

While determining the glyceride (monoglycerides, diglycerides and triglycerides) content in the reaction samples according to the standard UNE-EN 14105:2003, which involves an analysis by gas chromatography, an unexpected broad peak (Peak 2 of the chromatograms in Fig. 1) was observed under certain reaction conditions in the GC chromatogram. This peak, of 20.5–23.3 min chromatographic retention time, was composed of many overlapping peaks and increased with reaction temperature and treatment time (see Fig. 1), suggesting that it might arise from the thermal decomposition of fatty acid chains.

To verify this, the behaviour of the main unsaturated and saturated FAMEs (methyl oleate, linoleate and linolenate, and methyl palmitate, respectively) (see Table 1) generated during the transesterification reaction of soybean oil with supercritical methanol was studied, and their evolution was compared with that of Peak 2 in the chromatograms of Fig. 1.

Fig. 2 shows how methyl linoleate evolved with the reaction time at different temperatures. As observed, the yield of methyl linoleate, which is expressed, as for the rest of FAMEs, as the third part of the moles of the compound generated with respect to the moles of the initial triglycerides, increased continuously with the reaction time for temperatures lower than 300 °C, indicating that this compound was not thermally decomposed in this temperature range, even at long reaction times (90 min). Similar results were obtained by Imahara et al. [20] during the supercritical methanolysis of commercial methyl linoleate. This behaviour was identical to that observed in Fig. 1, in which it can be clearly appreciated that Peak 2 was not detected below 300 °C, even at long reaction times (90 min). Moreover, it was observed that at this temperature (300 °C) and above, the yield of methyl linoleate passed through a maximum, which was reached at shorter reaction times as the temperature applied increased; thus, the maximum yield of methyl linoleate was reached after 75–85 min at 300 °C/26 MPa, and after 50–65 and 5–15 min at 325 °C/35 MPa and 350 °C/43 MPa, respectively (times at which the triglycerides were already totally converted in all these reaction conditions [see Fig. 3]). This maximum seems to be a result of two competing phenomena: methyl linoleate production through transesterification and degradation through thermal decomposition. A clear maximum in the ester content was also observed by Vieitez et al. [21] during the supercritical ethanolysis of soybean oil at 350 °C in a continuous catalyst-free process. This behaviour again reflected the evolution of Peak 2 in Fig. 1, which began to appear at reaction times longer than 75 min at 300 °C/26 MPa, coinciding with the time at which the yield of methyl linoleate began to decline; moreover, the higher the temperature applied, the shorter the reaction time needed for this peak to appear. Thus, Peak 2 was first observed at 30 min (time at which the growth rate of methyl linoleate yield began to decrease [see Fig. 2]) at 325 °C/35 MPa, while it became evident before 15 min at 350 °C/43 MPa, coinciding with the decrease in the yield of methyl linoleate.

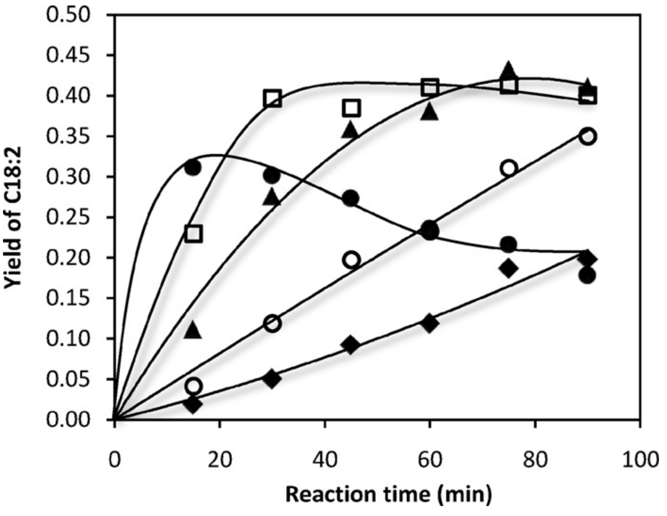

Fig. 2. Yield of methyl linoleate (C18:2) as a function of reaction time for temperatures of: ◆, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

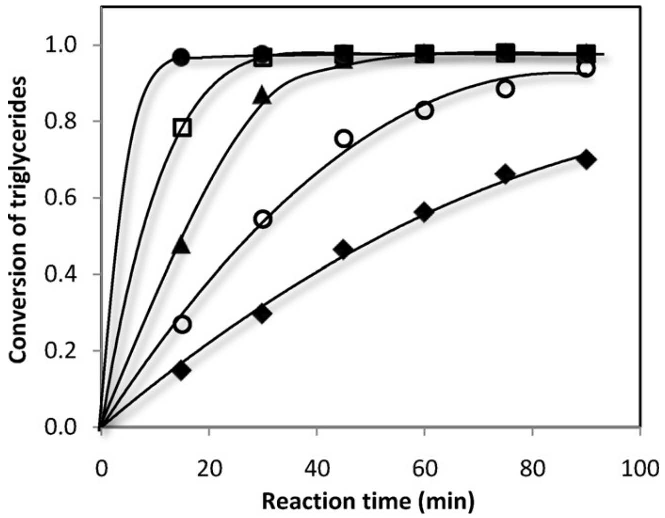

Fig. 3. Conversion of triglycerides as a function of reaction time for temperatures of: ◆, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

Fig. 2 also shows that, after the time at which the maximum of methyl linoleate was reached (when total conversion of triglycerides had already been achieved) for each temperature (300, 325 and 350 °C), the yield of this compound decreased (more slowly as the temperature fell), probably due to the thermal decomposition of methyl linoleate in the reaction conditions used, which was less intense as the temperature decreased. Moreover, the maximum reached at 300, 325 and 350 °C was always lower than the content of linoleic acid type fatty chains in the oil (53.1 mol%) (see Table 1) and was lower as the temperature increased, indicating again the existence of thermal decomposition reactions, which were more intense the higher the temperature applied. Thermal decomposition of methyl linoleate above 300 °C was also observed by He et al. [22] during the supercritical methanolysis of soybean oil; these authors found that the decrease of the yield of biodiesel above 300 °C was mainly due to the loss of unsaturated FAMEs which contain two or more double bonds.

Table 2
Peak 2-to-Peak 6 area ratio of the GC chromatograms in Fig. 1.

Reaction time (min)	Temperature (°C)				
	250 [12 MPa]	275 [18 MPa]	300 [26 MPa]	325 [35 MPa]	350 [43 MPa]
15	0.0	0.0	0.0	0.0	3.9
30	0.0	0.0	0.0	1.5	7.1
45	0.0	0.0	0.0	3.2	8.4
60	0.0	0.0	0.0	4.1	10.4
75	0.0	0.0	0.0	4.0	10.3
90	0.0	0.0	0.9	3.9	11.4

Furthermore, in Fig. 2 it was observed that at the highest temperatures applied (325 and 350 °C), the decrease in the post-maximum yield of methyl linoleate inexplicably slowed down after about 60 min of reaction. As can be seen from Table 2, which shows the values of the area ratio between Peak 2 and internal standard no. 2 (glyceryl tridecanoate) (Peak 6 in the top chromatogram of Fig. 1), this behaviour was the same as that observed for Peak 2 because the area ratio remained practically constant for reaction times longer than 60 min.

Fig. 4 shows how methyl linolenate behaved similarly to methyl linoleate; that is, it increased continuously with the reaction time for temperatures lower than 300 °C and passed through a maximum at this temperature and above. Moreover, the maximum reached at 300, 325 and 350 °C was always lower than the content of linolenic acid type fatty chain in the oil (7.2 mol%) (see Table 1), clearly indicating the thermal decomposition of methyl linolenate in these reaction conditions. Thermal degradation of methyl linolenate was also observed by other authors in similar conditions [20,21]. Therefore, the thermal decomposition products of this compound can also contribute to the formation of Peak 2 of the chromatograms in Fig. 1, although to a much lesser extent than methyl linoleate because the linolenic type fatty acid chain was present in small amounts in the soybean oil.

The only unsaturated FAME generated, which hardly decomposed in the experimental conditions tested and, therefore, would not have contributed to the formation of Peak 2, was the methyl oleate (see Fig. 5). The yield of this compound did not pass through a maximum during the reaction, but increased continuously with the reaction time for all temperatures studied, reaching a plateau at long reaction times at 300, 325 and 350 °C, when the triglycerides would have been completely converted; in addition, the higher the temperature applied, the greater the value of the yield attained at the plateau. Moreover, the greatest yield of methyl oleate reached at 350 °C was very close to the content of oleic acid type fatty chains in the soybean oil (24.4 mol%, the second most abundant) (see Table 1). Similar results were obtained by other authors in the same reaction conditions [20,21].

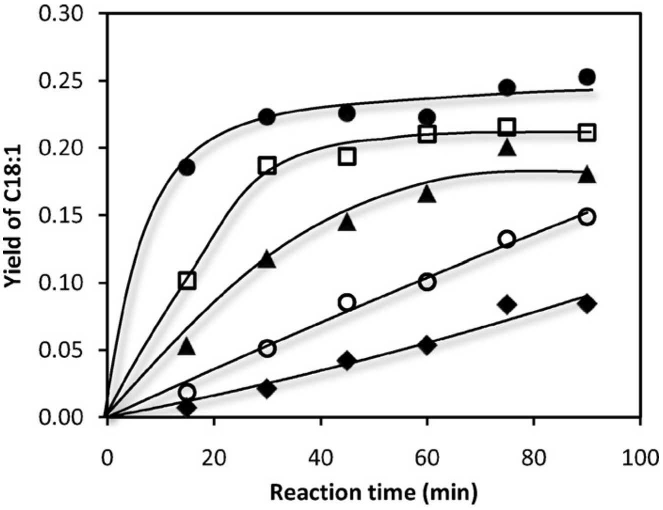

Fig. 5. Yield of methyl oleate (C18:1) as a function of reaction time for temperatures of: ♦, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

As regards methyl palmitate, Fig. 6 shows that, regardless of the temperature, its yield increased continuously with the reaction

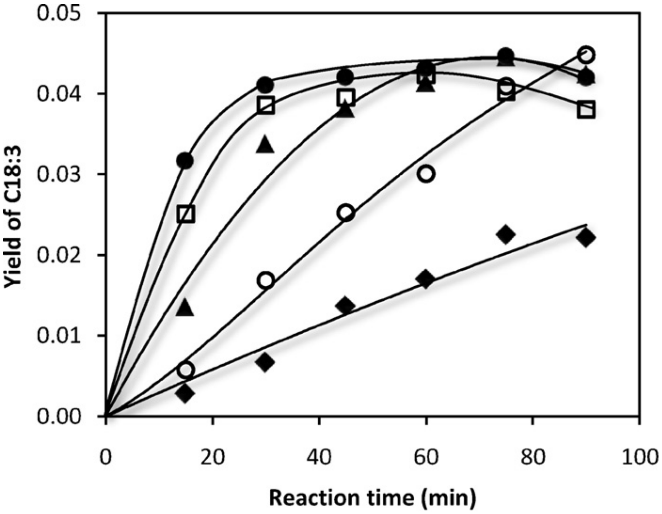

Fig. 4. Yield of methyl linolenate (C18:3) as a function of reaction time for temperatures of: ♦, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

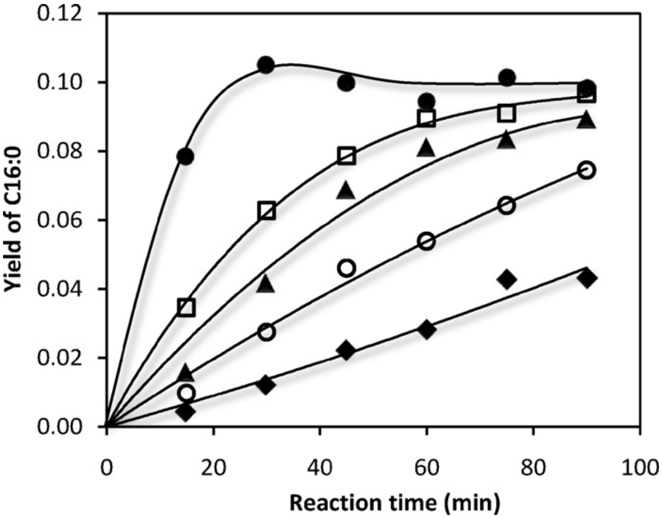

Fig. 6. Yield of methyl palmitate (C16:0) as a function of reaction time for temperatures of: ♦, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

time and, as expected, reached a plateau at long reaction times, when the triglycerides would have been completely converted (see Fig. 3); the only exception was at the highest temperature tested (350 °C), when the yield of methyl palmitate decreased slightly with the reaction time. This, together with the fact that the greatest yield of methyl palmitate reached (at the highest temperatures tested, 325 and 350 °C) was very close to the content of palmitic acid type fatty chains in the oil (11.1 mol%) (see Table 1), suggests that methyl palmitate was hardly decomposed in the range of experimental conditions tested [10,12]. It therefore generated hardly any decomposition product and would have contributed very little to the formation of Peak 2.

He et al. [22] showed that polyunsaturated FAMEs begin to be lost through side reactions at 300 °C, while Kusdiana and Saka [10,12] pointed out that saturated and polyunsaturated FAMEs only begin to disappear through thermal decomposition and dehydrogenation reactions at temperatures higher than 400 and 350 °C, respectively. In our study, the temperature at which decomposition reactions of the polyunsaturated FAMEs occurred (300 °C), was lower than that found by Kusdiana and Saka [10,12] and the same as that in He et al.'s study.

In order to confirm the existence of thermal decomposition reactions of the unsaturated fatty acid chains, the evolution of the molar ratio between mthyl linoleate and methyl palmitate (the main unsaturated and saturated FAMEs generated, respectively) was studied (see Fig. 7). The results showed that the molar ratio between these two FAMEs decreased with the reaction time at 300 °C/26 MPa and above: the higher the temperature, the lower the molar ratio. This clearly indicates that methyl linoleate disappeared during the reaction at temperatures of 300 °C and above (note that very little methyl palmitate disappeared in the reaction conditions tested), its disappearance being more intense at higher reaction temperatures. This behaviour may have been due to thermal decomposition reactions of the unsaturated fatty acid chains as well as isomerization of the *cis*-type double bonds into *trans*-type [20,21] at 300 °C/26 MPa and above, which were more intense at higher reaction temperatures. It can also be seen in Fig. 7 that below 300 °C the molar ratio between methyl linoleate and methyl palmitate remained practically constant during the reaction, tending to a value of 4.8 for long reaction times; moreover,

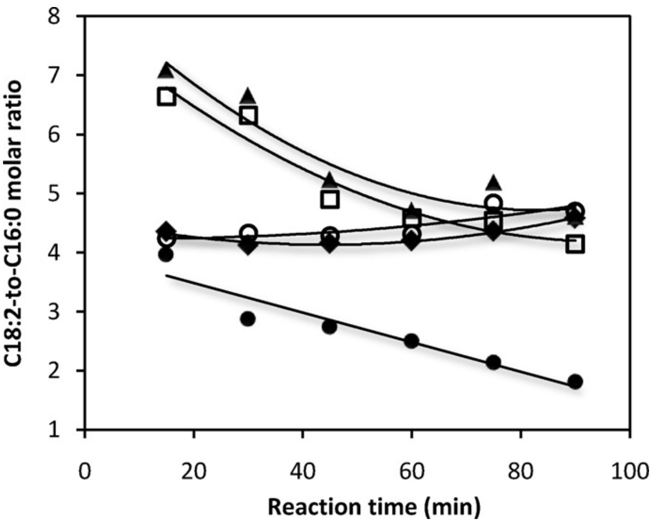

Fig. 7. Methyl linoleate (C18:2)-to-methyl palmitate (C16:0) molar ratio as a function of reaction time for temperatures of: ♦, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

Table 3
Mass balance in the reactor for supercritical methanol transesterification of soybean oil.

T (°C)	*t* (min)	ME[a]	MG[a]	DG[a]	Gly[a]	TG[a]	MeOH[a]	TG + MeOH[a]	ME + MG + DG + Gly[a]	Error (%)
250	15	38.9	5.3	106.4	0.9	149.0	4.3	153.30	151.4	1.2
	30	99.9	24.7	162.1	6.7	297.1	10.9	308.07	293.4	4.8
	45	189.8	54.5	210.8	29.4	462.6	20.8	483.44	484.5	−0.2
	60	238.0	78.9	220.7	44.6	560.4	26.1	586.49	582.3	0.7
	75	375.9	89.4	196.9	43.6	659.8	41.2	701.02	705.9	−0.7
	90	381.9	97.2	208.1	51.2	697.7	41.8	739.56	738.4	0.2
275	15	86.9	20.4	160.6	3.7	269.9	9.5	279.4	271.6	2.8
	30	234.4	79.0	214.8	37.9	544.0	25.7	569.7	566.1	0.6
	45	383.1	129.6	204.9	107.6	755.0	42.0	796.9	825.3	−3.6
	60	445.0	147.7	180.2	137.1	828.8	48.7	877.5	909.9	−3.7
	75	598.5	146.1	144.2	128.1	885.8	65.6	951.4	1016.9	−6.9
	90	661.0	147.5	105.4	167.5	939.9	72.4	1012.3	1081.4	−6.8
300	15	222.1	57.9	191.2	26.7	475.5	24.3	499.8	497.9	0.4
	30	523.4	122.6	149.1	145.4	865.7	57.3	923.1	940.5	−1.9
	45	664.8	135.8	71.9	176.6	957.9	72.8	1030.7	1049.0	−1.8
	60	721.6	121.3	41.1	223.7	973.2	79.0	1052.3	1107.8	−5.3
	75	757.6	99.1	39.0	191.4	975.5	83.0	1058.5	1087.1	−2.7
	90	777.6	90.1	32.2	231.7	974.1	85.2	1059.3	1131.6	−6.8
325	15	445.5	103.8	187.7	95.9	784.0	48.8	832.8	832.9	0.0
	30	774.5	122.0	51.9	157.2	967.9	84.8	1052.7	1105.8	−5.0
	45	790.8	64.5	30.3	225.1	976.6	86.6	1063.2	1110.7	−4.5
	60	836.2	37.8	29.2	235.3	977.5	91.6	1069.1	1138.5	−6.5
	75	833.3	35.6	25.5	255.8	979.7	91.3	1071.0	1150.2	−7.4
	90	820.1	27.7	23.3	262.8	977.6	89.8	1067.4	1134.0	−6.2
350	15	692.2	114.4	48.0	165.6	965.3	75.8	1041.1	1020.3	2.0
	30	761.8	29.8	9.5	217.1	972.4	83.4	1055.9	1018.2	3.6
	45	720.9	25.9	10.0	254.0	974.5	79.0	1053.4	1010.8	4.0
	60	680.4	23.3	8.7	195.2	974.8	74.5	1049.3	907.6	13.5
	75	736.5	23.6	9.9	197.3	976.5	80.7	1057.2	967.3	8.5
	90	703.3	18.2	9.9	171.5	973.7	77.0	1050.7	902.9	14.1

T = reaction temperature; *t* = reaction time; ME = methyl esters generated; MG = monoglycerides generated; DG = diglycerides generated; Gly = glycerine generated; TG = triglycerides converted; MeOH = theoretical methanol reacted; Error = [(TG + MeOH) − (ME + MG + DG + Gly)] × 100/(TG + MeOH).

[a] Expressed in mg/g of initial triglycerides.

this behaviour was practically the same whatever the temperature applied. Therefore, if one considers that the molar ratio between the fatty acid chains of linoleic and palmitic acid type of the commercial soybean oil used for the reaction is 4.8 (a value always equal to or slightly greater than any value obtained for the molar ratio between methyl linoleate and methyl palmitate), it is clear that no thermal decomposition of the fatty acid chains took place at temperatures below 300 °C.

Another way of demonstrating the thermal decomposition of the fatty acid chains during the transesterification reaction in supercritical conditions is based on the mass balance in the reactor (see Table 3). The balance was made taking into account that, in each experiment, the sum of the amount of triglycerides converted and the theoretical amount of methanol reacted (calculated from the amount of methyl esters generated) must be equal to the sum of the amounts of methyl esters, monoglycerides, diglycerides and glycerine generated. As can be seen, the results indicate that the mass balance in the reactor was, in general, correctly accomplished (negative errors lower than 7%). However, at 350 °C/43 MPa all errors were positive (the sum of the amounts of all the reaction products was lower than that of the reactants) and increased with the reaction time, reaching a value of 14.1 at 90 min, indicating that undesirable thermal decomposition reactions might have occurred, which agrees with the results reported by other authors [10,20].

Among the undesirable reactions of thermal degradation of the unsaturated fatty acid chains which could be produced are the oligomerization and polymerization of both the vegetable oil and the methyl esters generated [27]. The monounsaturated fatty acid methyl esters could essentially suffer thermal linear dimerization to form the acyclic structure of the dimers, while the polyunsaturated ones could originate a mixture of the monocyclic and six-membered cyclic dimers [28]. In addition, thermal cracking and olefinic bond isomerization (positional, geometrical and structural) reactions of the unsaturated fatty acid chains could be developed. However, as suggested by the correct mass balance achieved in the reactor in the best reaction conditions for this catalyst-free one-step supercritical process (a methanol-to-oil molar ratio of 43, a temperature of 325 °C and a reaction time of 60 min, which led to a yield of biodiesel of 84% [internal communication]), the extent of these adverse reactions was small; i.e., the methanolysis reaction of glycerides was strongly favoured in these reaction conditions. Therefore, the low content of side products (e.g., oligomers, polymers, isomers, thermal cracking products, etc.) in the biodiesel produced in the best reaction conditions should not affect its properties as a fuel.

Nevertheless, after applying the best reaction conditions in the one-step supercritical process, in which practically total conversion of triglycerides was reached, around 14 mol% of monoglycerides and diglycerides remained in the medium (internal communication). The only way to reduce the content of these glycerides, and thus increase the yield of biodiesel, is to raise the temperature and/or to lengthen the reaction time, which would inevitably lead to an increase in the thermal decomposition products from methyl esters. Therefore, to increase the yield of biodiesel without dangerously increasing the thermal decomposition reactions, other strategies should be considered for the non-catalytic synthesis of biodiesel, such as gradual heating in a tube reactor [22], continuous synthesis in a microtube reactor [29] or a two-step process with intermediate glycerol removal [30].

4. Conclusions

Due to the great similarity between the disappearance (as a result of thermal decomposition) of the main polyunsaturated FAMEs generated during the transesterification reaction in supercritical conditions and the formation of the Peak 2 detected chromatographically during the determination of glycerides in the reaction samples according to the standard UNE-EN 14105:2003, it can be concluded that Peak 2 in the GC chromatogram obtained was composed almost entirely of the thermal decomposition products of the unsaturated FAMEs which contain two or more double bonds.

Based on these results, since the highest yield of biodiesel (84%) for a methanol-to-oil molar ratio of 43 (optimal ratio) was achieved at a temperature of 325 °C (which corresponded to a pressure of 35 MPa) for a reaction time of 60 min, conditions in which thermal decomposition of the fatty acid chains was observed, it can be affirmed that even the best reaction conditions leading to the highest yield of biodiesel during the transesterification of soybean oil with supercritical methanol and not using catalysts, involve a certain degree of thermal decomposition of the unsaturated fatty acid chains with two or more double bonds.

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References

[1] C. Kiwjaroun, C. Tubtimdee, P. Piumsomboon, LCA studies comparing biodiesel synthesized by conventional and supercritical methanol methods, J. Cleaner Production 17 (2009) 143–153.

[2] B.K. Bala, Studies on biodiesels from transformation of vegetable oils for diesel engines, Energy Education Science and Technology 15 (2005) 1–43.

[3] S. Gryglewicz, Rapeseed oil methyl esters preparation using heterogeneous catalysts, Bioresource Technolgy 70 (1999) 249–253.

[4] S. Furuta, H. Matsuhashi, K. Arata, Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure, Catalysis Communication 5 (2004) 721–723.

[5] C.J. Shieh, H.F. Liao, C.C. Lee, Optimization of lipase-catalyzed biodiesel by response surface methodology, Bioresource Technolgy 88 (2003) 103–106.

[6] B. Freedman, E.H. Pryde, T.L. Mounts, Variables affecting the yields of fatty esters from transesterified vegetable oils, J. American Oil Chemists' Society 61 (1984) 1638–1643.

[7] F. Ma, L.D. Clements, M.A. Hanna, The effects of catalyst, free fatty acids, and water on transesterification of beef tallow, Transactions of the ASAE 41 (1998) 1261–1264.

[8] D. Kusdiana, S. Saka, Effects of water on biodiesel fuel production by supercritical methanol treatment, Bioresource Technology 91 (2004) 289–295.

[9] Y. Warabi, D. Kusdiana, S. Saka, Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols, Bioresource Technology 91 (2004) 283–287.

[10] S. Saka, D. Kusdiana, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel 80 (2001) 225–231.

[11] D. Kusdiana, S. Saka, Kinetics of transesterification in rapeseed oil to biodiesel fuels as treated in supercritical methanol, Fuel 80 (2001) 693–698.

[12] D. Kusdiana, S. Saka, Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol, J. Chemical Engineering of Japan 34 (2001) 383–387.

[13] E.S. Song, J.W. Lim, H.S. Lee, Y.W. Lee, Transesterification of RBD palm oil using supercritical methanol, J. Supercritical Fluids 44 (2008) 356–363.

[14] A. Demirbas, Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics, Energy Conversion and Management 47 (2006) 2271–2282.

[15] R.O. Dunn, Alternative jet fuels from vegetable-oils, Transactions of the ASAE 44 (2001) 1151–1157.

[16] A. Demirbas, Biodiesel from vegetable oils via transesterification in supercritical methanol, Energy Conversion and Management 43 (2002) 2349–2356.

[17] H. Han, W. Cao, J. Zhang, Preparation of biodiesel from soybean oil using supercritical methanol and CO_2 as co-solvent, Process Biochemistry 40 (2005) 3148–3151.

[18] W. Cao, H. Han, J. Zhang, Preparation of biodiesel from soybean oil using supercritical methanol and co-solvent, Fuel 84 (2005) 347–351.

[19] A. Demirbas, Biodiesel from sunflower oil in supercritical methanol with calcium oxide, Energy Conversion and Management 48 (2007) 937–941.

[20] H. Imahara, E. Minami, S. Hari, S. Saka, Thermal stability of biodiesel in supercritical methanol, Fuel 87 (2008) 1–6.

[21] I. Vieitez, C. da Silva, I. Alckmin, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Effect of temperature on the continuous synthesis of soybean esters under supercritical ethanol, Energy & Fuels 23 (2009) 558–563.
[22] H. He, T. Wang, S. Zhu, Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process, Fuel 86 (2007) 442–447.
[23] A. Demirbas, Production of biodiesel fuels from linseed oil using methanol and ethanol in non-catalytic SCF conditions, Biomass and Bioenergy 33 (2009) 113–118.
[24] P. Valle, A. Velez, P. Hegel, G. Mabe, E.A. Brignole, Biodiesel production using supercritical alcohols with a non-edible vegetable oil in a batch reactor, J. Supercritical Fluids 54 (2010) 61–70.
[25] G. Madras, C. Kolluru, R. Kumar, Synthesis of biodiesel in supercritical fluids, Fuel 83 (2004) 2029–2033.
[26] K.T. Tan, M.M. Gui, K.T. Lee, A.R. Mohamed, An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production, J. Supercritical Fluids 53 (2010) 82–87.
[27] M.M. Conceiçao, V.J. Fernandes, A.S. Araújo, M.F. Farias, I.M.G. Santos, A.G. Souza, Thermal and oxidative degradation of castor oil biodiesel, Energy & Fuels 21 (2007) 1522–1527.
[28] I.S. Patrikios, P.C. Patsalis, Monounsaturated fatty acid oligomerization is responsible for the agglutination activity of heated virgin olive oil, Food Research International 36 (2003) 985–990.
[29] C. da Silva, F. de Castillos, J.V. Oliveira, L.C. Filho, Continuous production of soybean biodiesel with compressed ethanol in a microtube reactor, Fuel Processing Technology 91 (2010) 1274–1281.
[30] S.A. D'Ippolito, J.C. Yori, M.E. Iturria, C.L. Pieck, C.R. Vera, Analysis of a two-step, noncatalytic, supercritical biodiesel production process with heat recovery, Energy & Fuels 21 (2007) 339–346.

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Synthesis of biodiesel from soybean oil using supercritical methanol in a one-step catalyst-free process in batch reactor

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ABSTRACT

The transesterification of soybean oil with supercritical methanol in a batch reactor with no added catalyst was investigated, studying the evolution of intermediate products (monoglycerides and diglycerides) as well as the conversion of triglycerides and the yield of fatty acid methyl esters and glycerol. Experiments were carried out in a temperature range of 250–350 °C (12–43 MPa) at reaction times of between 15 and 90 min for a methanol-to-oil molar ratio of 43:1. The best reaction conditions in this one-step supercritical process (325 °C/35 MPa and 60 min), in which triglyceride conversion was practically total, led to a maximum yield of fatty acid methyl esters of 84%. In these conditions an 8.1 wt% of monoglycerides and diglycerides remained in the medium. Although the use of more severe reaction conditions (longer reaction times and higher temperatures) reduced the content of these glycerides, the yield of methyl esters decreased due to their thermal decomposition.

1. Introduction

Worldwide interest in biodiesel has been increasing due to its potential to reduce the dependence on imported petroleum, to mitigate possible negative impacts of global climate change by lowering net CO_2 emissions from the transportation sector [1] and, not least, to tax incentives and publicity on the part of biodiesel advocates. In addition to the abovementioned attributes, engine testing programs have shown that biodiesel fueling typically leads to lower emissions of particulate matter, unburned hydrocarbons, and carbon monoxide [2,3]. Moreover, biodiesel is sulfur-free, and so catalytic after treatment systems are not needed [3].

Biodiesel is made from the triglycerides (TG) that exist in biomass, such as animal fats, plant oils (*e.g.*, corn, palm, rapeseed and soybean oils) and algae. However, current worldwide production of vegetable oil and animal fat is not sufficient to replace the use of liquid fossil fuel (maximum foreseen replacement percentage is *ca.* 20–25%) [4]. The transesterification reaction involved in biodiesel production can be alkali-catalyzed [5], acid-catalyzed [6] or enzyme-catalyzed [7]. An excess of methanol is necessary to shift the reaction to the right in order to achieve a high yield of fatty acid methyl esters (FAME).

Transesterification with homogeneous strong alkali catalysts is the most widely used technique in industry to produce biodiesel because of its obvious advantages, such as a shorter reaction time, a higher conversion rate, and a smaller amount of catalyst [8]. However, it is not suitable for use with oils with water and free fatty acid (FFA) contents higher than 0.06 wt% and 0.5 wt%, respectively, which lead to saponification and inferior biodiesel characteristics [9,10]. In addition, the use of a strong catalyst would need washing steps to be incorporated after the transesterification reaction to eliminate the dissolved catalyst.

Many solutions have been proposed for handling acidic feedstocks: (i) pre-neutralization of FFA (easily done but produces a lower net yield if the soaps are not recycled); (ii) pre-esterification of FFA with methanol or glycerol, catalyzed by strong acids (slow), followed by esterification in alkaline medium (fast); (iii) fully acid catalyzed esterification.

Another alternative to these processes is to carry out the reaction with supercritical methanol since the presence of water and FFA in the oil does not affect the progress of transesterification [11,12]. In addition, as the use of catalysts is not strictly necessary in supercritical conditions, catalyst-removal is not required after the process. This catalyst-free supercritical approach permits the mixture between methanol and oil to become a single homogeneous phase, thus accelerating transesterification because there is no interphase mass transfer to limit the reaction rate. It has been reported that the solubility parameter of methanol can be reduced under supercritical conditions and approximate that of vegetable oils at suitable temperatures and pressures [13].

Transesterification consists of three consecutive and reversible reactions [14,15] in which TG are converted stepwise to diglycerides (DG), monoglycerides (MG) and, finally, to glycerol, one mole of ester being liberated in each step. In order to achieve a high yield

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of fatty acid esters (biodiesel) an excess of methanol is required. The formation of alkyl esters from MG is believed to be the step that determines the reaction rate since MG are the most stable intermediate compounds [16]. After the reaction, the products consist of a mixture of fatty acid esters (the main reaction product), glycerol, alcohol, MG, DG, TG and thermal degradation products [17]. The presence of MG causes the biodiesel obtained to be cloudy (crystals), and so the standard UNE-EN 14214 limits its content to a maximum of 0.8 wt% in biodiesel. In general, impurities raise the cloud and pour points of biodiesel. This standard also limits the DG and TG content in biodiesel to a maximum of 0.2 wt% each.

There is an apparent contradiction in the literature between the different reaction conditions outlined by several authors to reach maximum biodiesel yield during supercritical methanol transesterification in batch reactors. The main operating parameters that influence the supercritical reaction in batch reactors are the temperature, the methanol-to-oil molar ratio and the reaction time. Other influencing variables are the operating pressure (directly related to the reaction temperature and the filling volume of the reactor) and the stirring rate of the reaction medium. The optimal methanol-to-oil molar ratio obtained by most of the authors is in the range 40:1–45:1 [18–21]. However, the optimum temperature and reaction time are between 280 and 400 °C, and between 4 and 30 min, respectively, depending on the type of batch reactor and the oil used [22,23]. In general, the FAME content achieved in optimal conditions has been very high (90–95%), but varies between 77 and 95% [22,23]. On the other hand, most authors have only analyzed the conversion to FAME or the yield of FAME, without reference to the evolution of the intermediate reaction products (MG and DG) and glycerol.

Therefore, the aim of the present study was to experimentally investigate the effect of the reaction temperature and time on the transesterification of refined soybean oil with supercritical methanol in a batch reactor with shaking at a methanol-to-oil molar ratio of 43:1 (optimal molar ratio) and no added catalysts. In this research the conversion of TG, the yield of FAME (biodiesel) and glycerol, as well as the evolution of the intermediate products (MG and DG) are determined in temperature and time ranges of 250–350 °C (which corresponds to pressures between 12 and 43 MPa) (above 350 °C the yield of biodiesel usually decreases) and 15–90 min, respectively. In addition, the degree of thermal degradation of the biodiesel obtained in different reaction conditions was also determined.

2. Materials and methods

2.1. Materials

A commercial refined soybean oil supplied by Lesieur Cristal (Roche Noires, Casablanca, Maroc), whose fatty acid composition is shown in Table 1, was used for this study. Anhydrous methanol was supplied by Panreac Química, S.A.U. (Castellar del Vallès, Barcelona, Spain), while methyl heptadecanoate, 1,2,4-butanetriol, 1,2,3-tricaproylglycerol (tricaprin), monoolein, diolein, triolein and glycerol were supplied by Sigma–Aldrich (Tres Cantos, Madrid, Spain) and used as standards.

Table 1
Fatty acid composition of commercial refined soybean oil.

Palmitic acid (C16:0)	10.2
Stearic acid (C18:0)	3.8
Oleic acid (C18:1)	24.7
Linoleic acid (C18:2)	53.5
Linolenic acid (C18:3)	7.2
Other acids	0.6
Total	100.0

2.2. Working method

The reaction was carried out in a batch shaken tank reactor (a stainless steel cylindrical autoclave of 83 ml capacity) to investigate the influence of the reaction temperature (250–350 °C) and reaction time (15–90 min). In each of the experiments, the reactor was loaded with 50 g of methanol–soybean oil mixture and introduced pneumatically by a mechanical arm into a smelted salt bath which permits the reaction mixture to reach the desired temperature in about 10 min. In all the experiments, the reaction time was taken to have started when the reactor was immersed in the salt bath. The reactor was continuously shaken orbitally (70 rpm) during the reaction, and, after removal from the salt bath, introduced in a water bath to stop the reaction. The product obtained was evaporated by rotavapor to remove the remaining methanol and stored in a refrigerator before analysis.

2.3. Analytical methods

The reaction was monitored by gas chromatography (GC/FID) to determine the content of glycerides (MG, DG and TG) and glycerine, and to analyse individual methyl esters. The apparatus used was a 3900 Varian gas chromatograph equipped with a CP 8400 Varian autosampler and coupled to an FID detector.

2.3.1. Analysis of glycerides and glycerine

The analysis of MG, DG, TG and glycerine was performed according to the standard UNE-EN 14105:2003. The principle of the method is based on the transformation of glycerides and glycerine into their respective silylated derivatives, which are more volatile. The silylation is carried out using N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) and in the presence of pyridine. The method requires two internal standard solutions: (a) n° 1, obtained by dissolving 50 mg of 1,2,4-butanetriol in 50 ml of pyridine in a volumetric flask; and (b) n° 2, obtained by dissolving 80 mg of 1,2,3-tricaproylglycerol (tricaprin) in 10 ml of pyridine in a volumetric flask.

100 mg of sample were weighed into a 10 ml vial, and then 80 μl of standard solution n° 1, 100 μl of standard solution n° 2 and 100 μl of MTSFA were added, avoiding contact with moisture. Subsequently, the vial was closed tightly, shaken vigorously and allowed to stand for 15 min at room temperature. Finally, 8 ml of heptane were added and an aliquot of 2 μl was injected into the gas chromatograph.

The chromatograph was fitted with a FactorFour VF-5ht capillary column (10 m × 0.32 mm, 0.1 μm film). Helium was used as carrier gas at a flow rate of 1 ml/min with a split ratio of 1:70. The temperature ramp of the oven was: 1 min at 50 °C, 15 °C/min to 180 °C, 7 °C/min to 230 °C, 10 °C/min to 370 °C and 5 min at 370 °C. The detector temperature was 380 °C and that of the injector 280 °C.

2.3.2. Analysis of methyl esters

To determine the individual methyl esters the standard UNE-EN 14103:2003 was applied. For this, 250 mg of sample were dissolved in 5 ml of standard solution (prepared in a volumetric flask by dissolving 500 mg of methyl heptadecanoate in 50 ml of heptane) in a 10 ml vial. Then, the vial was closed with a teflon cap and shaken vigorously. Finally, 2 μl of the solution obtained were injected into the gas chromatograph.

The apparatus was fitted with a CP-Wax 52-CB capillary column (30 m × 0.32 mm, 0.25 μm film). Helium was used as carrier gas at a flow rate of 1 ml/min with a split ratio of 1:50. The temperature of the oven was kept at 210 °C and that of the injector and detector at 250 °C. Analyses were performed in duplicate and the error in the determination of the FAME yield was ±2.6%.

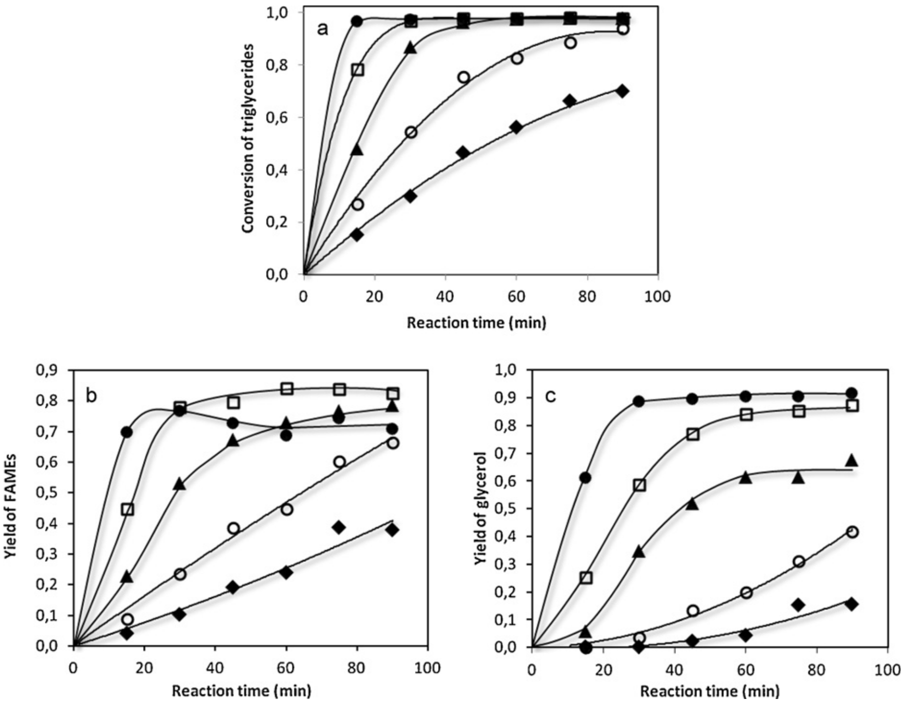

Fig. 1. Conversion of triglycerides (a), and yield of FAMEs (b) and glycerol (c) as a function of reaction time for temperatures of: ◆, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

2.3.3. Determination of thermal decomposition degree of fatty acid chains

Samples were treated with BF_3/MeOH according to the AOCS Official Method Ce 2-66 in order to derivatize glycerides (MG, DG and TG) and FFAs to the corresponding methyl esters, which were then analyzed by GC/FID as described above. In calculating the decomposition degree it was assumed that palmitic acid chains were resistant to degradation [17]. The decomposition degree (D), expressed as a percentage, was thus calculated according to the following equation, as described by Vieitez et al. [24]:

$$D = 100 \times \left[1 - \left(\frac{\sum P_i}{P_{16:0}}\right)_s \times \left(\frac{P_{16:0}}{\sum P_i}\right)_o\right]$$

where ΣP_i is the summation of the wt% of all fatty acid methyl esters, $P_{16:0}$ is the wt% of 16:0 methyl ester, and subscripts “s” and “o” indicate that the expressions between parentheses were evaluated taking into consideration the composition of the sample product and the original oil, respectively.

3. Results and discussion

The pressure reached in the reactor during experiments at 250, 275, 300, 325 and 350 °C was 12, 18, 26, 35 and 43 MPa, respectively, regardless of the reaction time. These values were higher than the critical pressure of methanol (8.09 MPa).

The following parameters were used to monitor the transesterification reaction: conversion of TG (moles of TG reacted/moles of initial TG), yield of FAME (third of the moles of FAME generated/moles of initial TG), yield of glycerol (moles of glycerol generated/moles of initial TG), yield of MG (moles of MG generated/moles of initial TG), and yield of DG (moles of DG generated/moles of initial TG).

The conversion of TG as a function of reaction time is shown in Fig. 1a for different reaction temperatures. As observed, the conversion of TG increased continuously with the reaction time for temperatures lower than 300 °C. Moreover, at this temperature and above, the conversion of TG reached a plateau of around 98%: the higher the temperature, the shorter the time needed to reach the plateau. Thus, this plateau was reached after 56 min at 300 °C, and after 33 and 15 min at 325 and 350 °C, respectively.

As expected, the higher the TG conversion, the greater the FAME yield at temperatures of up to 300 °C, although the FAME yield was always lower than the conversion (see Fig. 1b). This behavior was probably due, as indicated below, to the formation of intermediate products such as MG and DG. At temperatures above 300 °C, the yield of FAME passed through a maximum. The maximum reached at 325 °C (84% yield of FAME) was higher than that obtained at 350 °C (70% yield of FAME), and was reached at a longer reaction time (60–75 min at 325 °C vs. 20–30 min at 350 °C). The fact that the yield of FAME decreased at long reaction times was probably due, as discussed below, to the thermal degradation of the polyunsaturated fatty acid methyl esters generated [17].

As indicated by most authors, high yields of biodiesel can be obtained at short reaction times. For instance, Kusdiana and Saka [25] obtained a yield of methyl esters of 95 wt% from rapeseed oil in about 4 min in a batch reactor, while Minami and Saka [26] reported yields of around 90 wt% in 30 min for the methyl esterification of oleic acid in a continuous tubular reactor, and He et al. [27] achieved a 77 wt% yield during soybean oil transesterification with supercritical methanol for a reaction time of 25 min. In our case, the maximum yield of FAME (84%) was obtained at longer reaction times (60–75 min). Moreover, the best temperature obtained in the present study (325 °C) was lower than that reported by most authors [12,18,21,25,28], who point to 350–360 °C as the best reaction temperature, and the same as that mentioned by Trentin et al. [29] during the supercritical ethyl transesterification of soybean oil in a microtube reactor using carbon dioxide as co-solvent.

The evolution of glycerol, which is shown in Fig. 1c, was very similar to that of conversion of TG: the yield of glycerol increased continuously with the reaction time for all the temperatures studied and reached a plateau at 300, 325 and 350 °C, when the TG would have been completely converted; however, the higher the temperature used, the greater the yield of glycerol attained at the

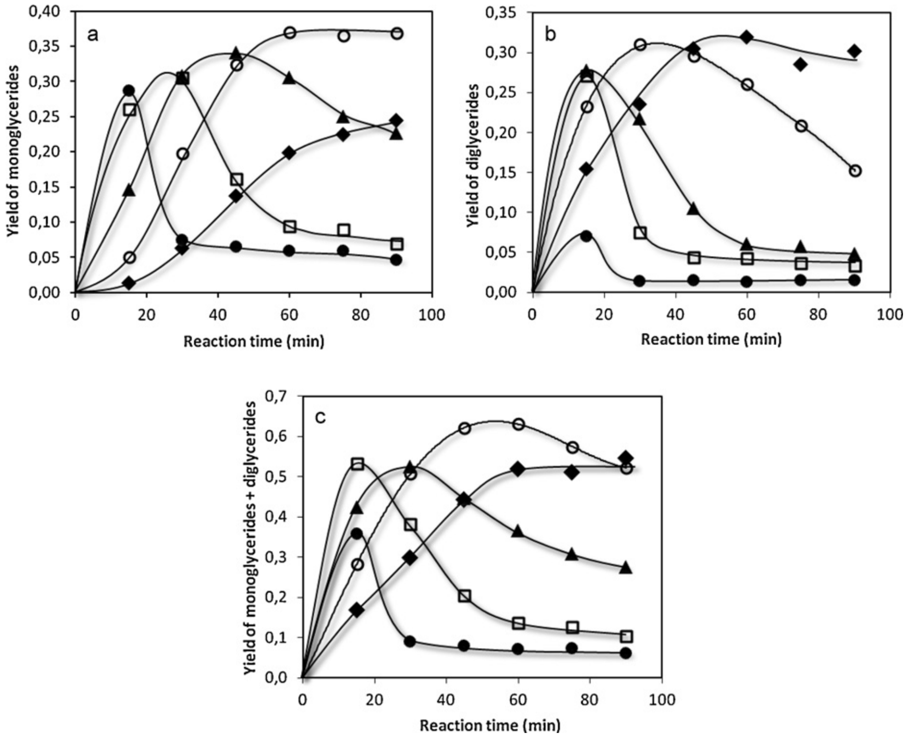

Fig. 2. Yield of monoglycerides (a), diglycerides (b) and monoglycerides + diglycerides (c) as a function of reaction time for temperatures of: ♦, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

plateau. Thus, a 65% yield was obtained at 300 °C, and 87 and 91% at 325 and 350 °C, respectively. The yield of glycerol was always lower than the conversion of TG, which, again, may be due to the presence in the medium of intermediate products (MG and DG) (see below). Moreover, the difference observed for long reaction times between the conversion of TG and the yield of glycerol decreased considerably with temperature, indicating that the disappearance of these intermediate products was strongly affected by temperature. The fact that the yield of glycerol did not fall with the reaction time at any of the temperatures used indicated that glycerol was not decomposed in the reaction conditions tested.

Intermediate products (MG and DG) were generated during the process, the evolution of which is shown in Fig. 2. The yield of MG (see Fig. 2a) increased with reaction time at 250 and 275 °C, and seemed to reach a plateau of 37% yield at 275 °C. However, the yield of MG passed through a maximum at 300 °C and above, which was reached at shorter reaction times as the temperature increased; thus, a 34% maximum yield of MG was reached after 45 min at 300 °C, while maxima of 31 and 29% were obtained after 26 and 15 min at 325 and 350 °C, respectively. Maxima for the concentration of MG were also obtained by Vieitez et al. [24] during the supercritical ethanol transesterification of refined soybean oil; however, these maxima were lower than those reported in this study. After reaching a maximum, and for long reaction times, the yield of MG seemed to decrease very slowly, the higher the temperature the lower the minimum yield reached. Thus, for a 90 min reaction time a 4.5% minimum yield of MG was obtained at 350 °C, while at 325 °C the minimum yield was of 6.5%. Therefore, it can be claimed that the only way to reduce the MG content in the medium is by increasing the temperature of the process.

As regards the yield of DG (see Fig. 2b), this passed through a maximum of between 27 and 32% for all the temperatures studied, the only exception being at 350 °C at which a 7% maximum yield was observed. After the maximum, the yield of DG decreased to a minimum value, which remained constant for long reaction times and which was lower the higher the temperature used. Thus, the minimum yield attained at 350, 325 and 300 °C was 1.7, 3.3 and 4.9%, respectively. Therefore, and as indicated for MG, the only way to reduce the DG content is by increasing the temperature. As expected, whatever the temperature, the maximum of DG was reached at shorter reaction times than that of MG, behavior that is typical in reactions that develop in successive steps, such as the three-step transesterification of TG with methanol.

As observed in Fig. 2c, the yield of MG + DG also passed through a maximum at all temperatures. The maximum reached at 250, 275, 300 and 325 °C was between 53 and 63%. Once the maximum was passed, and for long reaction times, the yield of MG + DG tended towards a minimum value, which was lower at higher temperatures. Thus, the minimum amount of MG plus DG (corresponding to a minimum yield of 5.5%) attained for this one-step supercritical process was obtained at 350 °C.

According to the standard UNE-EN 14214, the maximum content of MG, DG and TG in the biodiesel produced must be lower than 0.8, 0.2 and 0.2 wt%, respectively. This standard also prescribes the minimum content of FAME in the product, which should be above 96.5 wt%. As can be seen in Table 2, the content of these glycerides (MG, DG and TG) in the product obtained in different conditions was always higher than the maximum established by the standard. Around 2.5–3.5 wt% of TG remained in the medium even in the most severe reaction conditions. The minimum content of MG (1.77 wt%) and DG (0.97 wt%) was obtained at 350 °C and 90 min; in these conditions, the content of FAME was low (68.55 wt%), which may be due to the thermal degradation of the fatty acid chains. However, in the conditions leading to the highest FAME content [87.65 wt%, a lower value than the minimum indicated by the standard (96.5 wt%), at 325 °C and 75 min], the MG and DG content was 4.06 and 2.91 wt%, respectively. Therefore, the product obtained in this one-step catalyst-free supercritical process does not meet the specifications of the standard.

If the yield of FAME and glycerol is represented with respect to the conversion of TG, we obtain Fig. 3. It can be seen that the FAME (Fig. 3a) and glycerol (Fig. 3b) yields evolved very similarly

Table 2
Content of glycerides and methyl esters (wt%) in the product (ester phase) in different reaction conditions.

T (°C)	*t* (min)	MGC	DGC	TGC	MEC
250	15	0.52	10.44	83.53	3.81
	30	2.38	15.58	67.55	11.61
	45	5.28	20.39	52.00	19.40
	60	7.43	20.78	41.38	27.61
	75	9.01	19.84	34.26	36.82
	90	9.76	20.88	30.33	38.32
275	15	1.99	15.65	71.14	8.97
	30	7.66	20.85	44.25	24.82
	45	13.40	21.19	25.34	39.62
	60	15.96	19.47	18.51	46.95
	75	15.80	15.60	12.35	57.91
	90	16.38	11.71	6.68	67.10
300	15	5.67	18.74	51.40	21.77
	30	14.10	17.15	15.44	55.53
	45	16.49	8.73	5.11	71.76
	60	15.13	5.13	3.34	78.09
	75	13.90	5.47	3.44	79.11
	90	10.62	3.79	3.06	83.00
325	15	10.79	19.50	22.44	46.28
	30	14.53	6.19	3.82	76.08
	45	8.06	3.78	2.92	83.35
	60	4.57	3.53	2.72	85.77
	75	4.06	2.91	2.57	87.65
	90	3.31	2.79	2.68	86.14
350	15	12.19	5.12	3.69	73.74
	30	3.27	1.04	3.02	83.49
	45	2.81	1.08	2.77	78.15
	60	2.77	1.04	3.01	74.93
	75	2.40	1.01	2.39	72.61
	90	1.77	0.97	2.57	68.55

T = operating temperature; *t* = reaction time; MGC = monoglyceride content; DGC = diglyceride content; TGC = triglyceride content; MEC = methyl ester content.

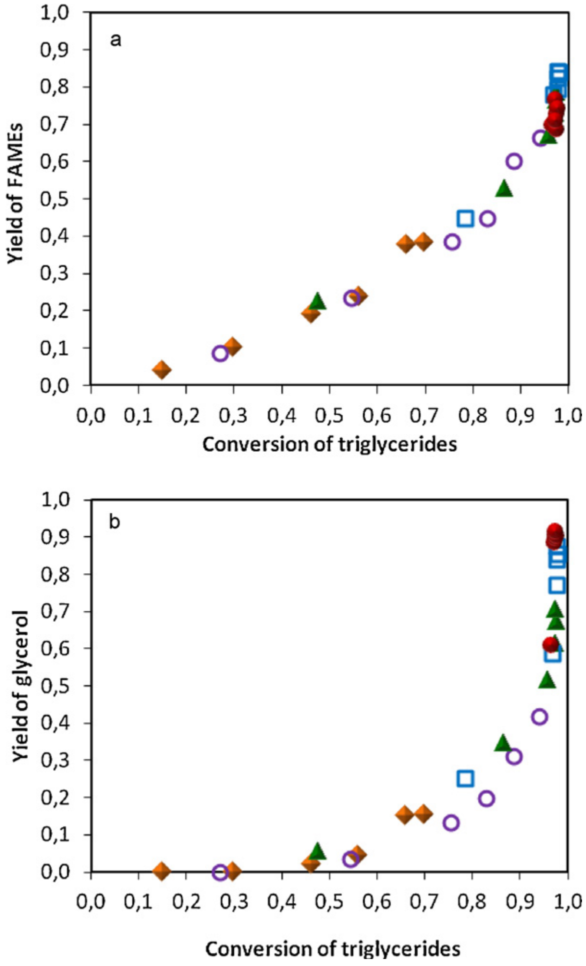

Fig. 3. Yield of FAMEs (a) and glycerol (b) as a function of triglyceride conversion for temperatures of: ◆, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ● 350 °C (43 MPa).

regardless of the temperature and reaction time; *i.e.*, for any combination of temperature and reaction time leading to the same conversion of TG, practically the same yield of FAME and glycerol was obtained. The only exception was for the glycerol yield at 275 °C and for TG conversions above 70%, for which values somewhat lower were obtained.

A similar result was obtained for the evolution of MG and DG with respect to the conversion of TG (see Fig. 4): for a given value of the conversion of TG, practically the same yield of MG (Fig. 4a) and DG (Fig. 4b) was obtained, whatever the combination of temperature and reaction time used. As in the case of FAME, the only exception was obtained for the MG yield at 275 °C and for conversions of TG above 70%; in these conditions, a somewhat higher value of the yield of MG was obtained, which coincides with the fact that a lower yield of glycerol was obtained at 275 °C (see Fig. 3b).

For conversions of TG above 93%, the yield of DG and, especially, that of MG, decreased drastically with the conversion (see Fig. 4a and b) leading to a large increase in the yield of glycerol and FAME (see Fig. 3a and b). Therefore, as expected, to achieve a very high yield of biodiesel it is necessary to reach TG conversions higher than 98%.

During the synthesis of biodiesel from refined soybean oil with supercritical methanol, both in a batch reactor and in a tube reactor, it has been qualitatively demonstrated that the thermal decomposition of FAME occurs at 300 °C and above [17,27]. In order to verify this, the decomposition degree of the fatty acid chains was quantified using the method described by Vieitez et al. [24]. As shown in Fig. 5, no thermal decomposition was observed at 250 and 275 °C, regardless of the reaction time. In addition, thermal degradation of fatty acid chains began to be evident at 300 °C at reaction times longer than 75 min, while at 325 °C thermal degradation became visible from 30 min. However, at 350 °C thermal degradation of the fatty acid chains occurred practically from the beginning. Once degradation was observed at a given temperature, the decomposition degree increased with the reaction time; therefore, maximum decomposition degrees of 3.2, 11.6 and 27.7% were obtained after 90 min at 300, 325 and 350 °C, respectively. The same trends were observed with the temperature for a given reaction time, and the undesirable thermal decomposition reactions were more intense as the temperature increased. All these results agree with that reported by Vieitez et al. [24,30] during the supercritical ethanol transesterification of refined soybean oil in a tubular reactor. Moreover, since only polyunsaturated FAME (methyl linoleate and linolenate) suffer thermal degradation between 300 and 350 °C [17,27], the decomposition degree observed corresponded exclusively to the disappearance of the linoleic and linolenic type fatty acid chains.

These results coincide exactly with those reported by Quesada-Medina and Olivares-Carrillo [17] during the supercritical transesterification of soybean oil with supercritical methanol. While determining the glyceride content in the reaction samples according to the standard UNE-EN 14105:2003, which involves analysis by gas chromatography, these authors observed the appearance of an unexpected broad chromatographic peak, composed of many overlapping peaks, that might correspond to the thermal degradation products. The evolution observed for the decomposition degree was the same as that observed for this peak, clearly indicating that this peak was composed of the thermal decomposition products.

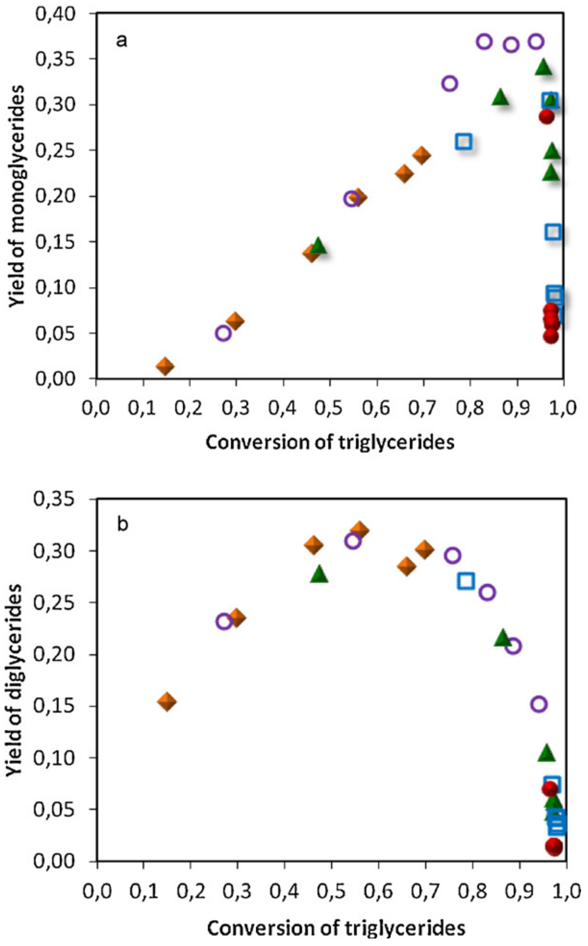

Fig. 4. Yield of monoglycerides (a) and diglycerides (b) as a function of triglyceride conversion for temperatures of: ◆, 250 °C (12 MPa); ○, 275 °C (18 MPa); ▲, 300 °C (26 MPa); □, 325 °C (35 MPa); ●, 350 °C (43 MPa).

Among the undesirable reactions of thermal degradation of the unsaturated fatty acid chains which could be produced are the oligomerization and polymerization of both the vegetable oil and the methyl esters generated [31]. The monounsaturated fatty acid methyl esters could, essentially, suffer thermal linear dimerization to form the acyclic structure of the dimers, while the polyunsaturated ones could originate a mixture of the monocyclic and six-membered cyclic dimers [32]. In addition, thermal cracking and olefinic bond isomerization (positional, geometrical and structural) reactions of the unsaturated fatty acid chains could be developed [33].

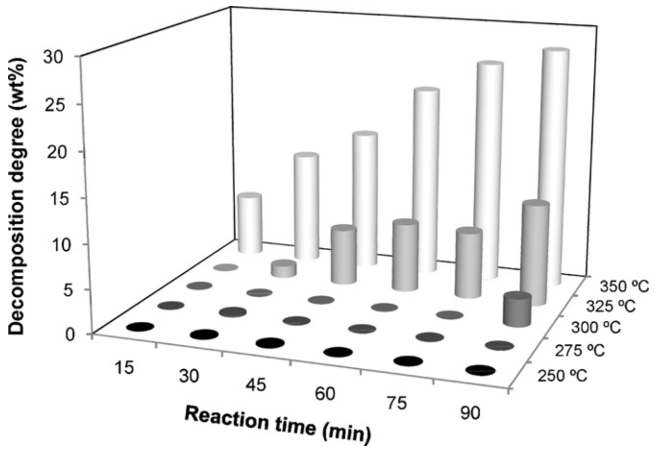

Fig. 5. Decomposition degree of fatty acid chains as a function of reaction time and temperature.

The maximum yield of FAME that can be obtained without causing thermal degradation of fatty acid chains (76.2%) was attained at 300 °C and 75 min. Substantial reaction yields (70%), along with very low levels of decomposition of fatty chains, were also obtained by Silva et al. [34] during supercritical ethanol transesterification of soybean oil in a microtube reactor. However, some authors carried out the process in more severe conditions (400 °C, 300 bar and 6 min of reaction time), using methanol-to-triglyceride molar ratios of 3:1–9:1 (significantly lower than optimal); under these conditions, thermal decomposition products of FAME and glycerol are generated and are incorporated, as valuable components, to the fuel [35,36].

In order to increase the yield of biodiesel above 84% the content of MG and DG needs to be reduced. The only way to do that is to raise the temperature or lengthen the reaction time, which would inevitably lead to an appreciable increase in the thermal decomposition products. Therefore, to increase the yield of FAME without dangerously increasing the thermal decomposition reactions, other strategies should be considered for the non-catalytic synthesis of biodiesel, such as gradual heating in a tube reactor [27] or a two-step process with intermediate glycerol removal [37].

4. Conclusions

The results obtained in this work demonstrate that in the one-step supercritical methanolysis of refined soybean oil, the methyl ester content of the product can be maximized at different reaction temperatures and times. The best reaction conditions leading to the highest yield of FAME (84%, equivalent to an 85.8 wt% in the ester phase) were a temperature of 325 °C (which corresponds to a pressure of 35 MPa) and a reaction time of 60 min. In these conditions, practically total conversion of TG was reached; however, 8.1 wt% of MG and DG remained in the medium and a 7.9 wt% decomposition of fatty acid chains was observed. The only way to reduce the content of these glycerides in this catalyst-free one-step supercritical process, and thus increase the yield of biodiesel, is to raise the temperature, which would inevitably lead to an appreciable increase in the thermal decomposition products.

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References

[1] C. Carraretto, A. Macor, A. Mirandola, A. Stoppato, S. Tonon, Biodiesel as alternative fuel: experimental analysis and energetic evaluations, Energy 29 (2004) 2195–2211.
[2] B.K. Barnwal, M.P. Sharma, Prospects of biodiesel production from vegetable oils in India, Renewable and Sustainable Energy Reviews 9 (2005) 363–378.
[3] M. Balat, H. Balat, A critical review of bio-petrodiesel as a vehicular fuel, Energy Conversion and Management 49 (2008) 2727–2741.
[4] B.K. Bala, Studies on biodiesels from transformation of vegetable oils for diesel engines, Energy Education Science and Technology 15 (2005) 1–43.
[5] S. Gryglewicz, Rapeseed oil methyl esters preparation using heterogeneous catalysts, Bioresource Technology 70 (1999) 249–253.
[6] S. Furuta, H. Matsuhashi, K. Arata, Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure, Catalysis Communications 5 (2004) 721–723.
[7] C.J. Shieh, H.F. Liao, C.C. Lee, Optimization of lipase-catalyzed biodiesel by response surface methodology, Bioresource Technology 88 (2003) 103–106.
[8] D.Y.C. Leung, X. Wu, M.K.H. Leung, A review on biodiesel production using catalyzed transesterification, Applied Energy 87 (2010) 1083–1095.

[9] B. Freedman, E.H. Pryde, T.L. Mounts, Variables affecting the yields of fatty esters from transesterified vegetable oils, Journal of American Oil Chemists' Society 61 (1984) 1638–1643.

[10] F. Ma, L.D. Clements, M.A. Hanna, The effects of catalyst, free fatty acids, and water on transesterification of beef tallow, Transactions of the ASAE 41 (1998) 1261–1264.

[11] Y. Warabi, D. Kusdiana, S. Saka, Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols, Bioresource Technology 91 (2004) 283–287.

[12] D. Kusdiana, S. Saka, Effects of water on biodiesel fuel production by supercritical methanol treatment, Bioresource Technology 91 (2004) 289–295.

[13] N. Deslandes, V. Bellenger, F. Jaffiol, J. Verdu, Solubility parameters of a polyester composite material, Journal of Applied Polymer Science 69 (1998) 2663–2671.

[14] B. Freedman, R.O. Butterfield, E.H. Pryde, Transesterification kinetics of soybean oil, Journal of American Oil Chemists' Society 63 (1986) 1375–1380.

[15] A.W. Schwab, M.O. Bagby, B. Freedman, Preparation and properties of diesel fuels from vegetable oils, Fuel 66 (1987) 1372–1378.

[16] F. Ma, M.A. Hanna, Biodiesel production: a review, Bioresource Technology 70 (1999) 1–15.

[17] J. Quesada-Medina, P. Olivares-Carrillo, Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol, Journal of Supercritical Fluids 56 (2011) 56–63.

[18] E.S. Song, J.W. Lim, H.S. Lee, Y.W. Lee, Transesterification of RBD palm oil using supercritical methanol, Journal of Supercritical Fluids 44 (2008) 356–363.

[19] A. Demirbas, Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics, Energy Conversion and Management 47 (2006) 2271–2282.

[20] P. Valle, A. Velez, P. Hegel, G. Mabe, E.A. Brignole, Biodiesel production using supercritical alcohols with a non-edible vegetable oil in a batch reactor, Journal of Supercritical Fluids 54 (2010) 61–70.

[21] G. Madras, C. Kolluru, R. Kumar, Synthesis of biodiesel in supercritical fluids, Fuel 83 (2004) 2029–2033.

[22] R. Sawangkeaw, K. Bunyakiat, S. Ngamprasertsith, A review of laboratory-scale research on lipid conversion to biodiesel with supercritical methanol (2001–2009), Journal of Supercritical Fluids 55 (2010) 1–13.

[23] M.M. Gui, K.T. Lee, S. Bhatia, Supercritical ethanol technology for the production of biodiesel: process optimization studies, Journal of Supercritical Fluids 49 (2009) 286–292.

[24] I. Vieitez, C. Silva, I. Alkimim, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Effect of temperature on the continuous synthesis of soybean esters under supercritical ethanol, Energy & Fuels 23 (2009) 558–563.

[25] D. Kusdiana, S. Saka, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel 80 (2001) 225–231.

[26] E. Minami, S. Saka, Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process, Fuel 85 (2006) 2479–2483.

[27] H. He, T. Wang, S. Zhu, Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process, Fuel 86 (2007) 442–447.

[28] K.T. Tan, K.T. Lee, A.R. Mohamed, Production of FAME by palm oil transesterification via supercritical methanol technology, Biomass and Bioenergy 33 (2009) 1096–1099.

[29] C.M. Trentin, A.P. Lima, I.P. Alkimim, C. Silva, F. Castilhos, M.A. Mazutti, J.V. Oliveira, Continuous catalyst-free production of fatty acid ethyl esters from soybean oil in microtube reactor using supercritical carbon dioxide as co-solvent, Journal of Supercritical Fluids 56 (2011) 283–291.

[30] I. Vieitez, C. Silva, I. Alckmin, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Continuous catalyst-free methanolysis and ethanolysis of soybean oil under supercritical alcohol/water mixtures, Renewable Energy 35 (2010) 1976–1981.

[31] M.M. Conceiçao, V.J. Fernandes, A.S. Araújo, M.F. Farias, I.M.G. Santos, A.G. Souza, Thermal and oxidative degradation of castor oil biodiesel, Energy & Fuels 21 (2007) 1522–1527.

[32] I.S. Patrikios, P.C. Patsalis, Monounsaturated fatty acid oligomerization is responsible for the agglutination activity of heated virgin olive oil, Food Research International 36 (2003) 985–990.

[33] H. Imahara, E. Minami, S. Hari, S. Saka, Thermal stability of biodiesel in supercritical methanol, Fuel 87 (2008) 1–6.

[34] C. Silva, F. de Castilhos, J.V. Oliveira, L.C. Filho, Continuous production of soybean biodiesel with compressed ethanol in a microtube reactor, Fuel Processing Technology 91 (2010) 1274–1281.

[35] A. Deshpande, G. Anitescu, P.A. Rice, L.L. Tavlarides, Supercritical biodiesel production and power cogeneration: technical and economic feasibilities, Bioresource Technology 101 (2010) 1834–1843.

[36] V.F. Marulanda, G. Anitescu, L.L. Tavlarides, Biodiesel fuels through a continuous flow process of chicken fat supercritical transesterification, Energy & Fuels 24 (2010) 253–260.

[37] S.A. D'Ippolito, J.C. Yori, M.E. Iturria, C.L. Pieck, C.R. Vera, Analysis of a two-step, noncatalytic, supercritical biodiesel production process with heat recovery, Energy & Fuels 21 (2007) 339–346.

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Thermal decomposition of fatty acid chains during the supercritical methanol transesterification of soybean oil to biodiesel

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ABSTRACT

The thermal decomposition of fatty acid chains was investigated in different reaction conditions [temperature, reaction time and methanol-to-oil molar ratio ranges of 250–350 °C, 15–90 min and 13:1 to 53:1, respectively] during the transesterification of refined soybean oil using supercritical methanol in a batch reactor. No decomposition was observed at 250 and 275 °C, regardless of the reaction time and methanol-to-oil molar ratio used. However, for practically all the molar ratios tested decomposition became evident at 300 °C when the reaction time was longer than 60 min, whilst at 325 and 350 °C similar behavior was observed almost from the first moments of the reaction (15 min). The molar ratio favored the formation of both saturated and unsaturated fatty acid methyl esters and had some protective effect on the thermal decomposition of the polyunsaturated esters. A new method for determining the degree of decomposition is proposed based on the area of a new chromatographic peak detected during the analysis of the reaction samples according to the standard UNE-EN 14105:2003.

1. Introduction

The severe reaction conditions needed for the uncatalyzed synthesis of biodiesel using supercritical methanol [1] can lead to the thermal decomposition of (i) the triglycerides present in the oil, (ii) the fatty acid methyl esters generated during the reaction, (iii) the intermediate reaction products (monoglycerides and diglycerides), and (iv) the main byproduct of the process (glycerol), resulting in most cases in lower yields of biodiesel than expected [2].

Maintaining the thermal stability of fatty acid methyl esters is one of the most important concerns in supercritical high-yield biodiesel production. Thermal decomposition reactions of fatty acid methyl esters during supercritical transesterification were first indicated in Kusdiana and Saka's research in 2001. These researchers observed that unsaturated and saturated fatty acid methyl esters begin to decompose at 350 and 400 °C, respectively [3,4]. However, He et al. [5] later pointed out that unsaturated methyl esters containing two or more double bonds (methyl linoleate and linolenate) decomposed above 300 °C, while Shin et al. [6] showed that their degradation occurred from 330 °C. Moreover, Imahara et al. [7] observed that saturated fatty acid methyl esters (methyl palmitate and stearate) were stable at 300 °C or below, becoming unstable at 350 °C, while Shin et al. [6] specified that (i) methyl palmitate remained almost stable at 400 °C or below, and (ii) methyl stearate was stable below 350 °C and decomposed slightly when the temperature rose to 375 °C. In the case of methyl oleate (the main monounsaturated fatty acid methyl ester generated from most of vegetable oils), it began to be unstable at 375 °C [6]. Therefore, it can be concluded that the shorter the chain length of fatty acid methyl ester and the more saturated the chain, the higher its thermal stability in supercritical methanol.

The thermal stability of fatty acid methyl esters was also investigated in supercritical methyl acetate. Thus, Niza et al. [8] observed that the thermal degradation of methyl oleate was only significant at 390 °C and above, while methyl linoleate degraded significantly even at 330 °C.

Among the undesirable reactions of thermal decomposition of the fatty acid chains that can occur during the supercritical process at temperatures above 300–325 °C are (i) oligomerization and polymerization of both the triglycerides and the unsaturated fatty acid methyl esters generated [9], (ii) linear dimerization of the monounsaturated (to form the acyclic structure of the dimers) and polyunsaturated (to form a mixture of monocyclic and six-membered cyclic dimers) fatty acid methyl esters [10], (iii) positional, geometrical and structural isomerization of the olefinic double bonds present in the unsaturated fatty acid chains, basically *cis*/*trans* isomerization [6,7,11], (iv) hydrogenation of the above mentioned olefinic double bonds [6], (v) thermal cracking of the saturated fatty acid chains (to form methyl esters of lower molecular weight, 1-alkenes and n-alkanes; this kind of decomposition product is typically generated during the radical chain scission processes in polymer pyrolysis) [6], and (vi) thermal cracking of the

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unsaturated fatty acid chains (to form saturated and unsaturated methyl esters in the range of C8–C14, arising from the breaking of the olefinic double bonds) [6,11,12].

Glycerol, which is formed as a byproduct of the transesterification reaction and has become a waste problem, also decomposes during the supercritical transesterification reaction, leading to low molecular weight compounds (acrolein, acetaldehyde, acetic acid, alcohols such as propanol, etc.), polyglycerols (usually diglycerol-related compounds), methyl glycerol ethers (mono-, di- or tri-methyl glycerol) and water [12–14]. Water can react further with the glycerides of the reacting mixture to form free fatty acids, thus increasing the acidity of the product; at longer reaction times the acids can be converted into methyl esters again [13].

Several authors [12,15–18] have observed that if the supercritical process is carried out at temperatures as high as 350–450 °C, pressures of 100–400 bar, short reaction times (3–10 min) and moderate alcohol molar ratios (3:1 to 12:1), then all of the formed glycerol decomposes into the above mentioned compounds, which remain blended within the biodiesel fuel forming an homogeneous liquid phase; in this way, the fuel amount can be increased by more than 10 wt% [13,15,16]. In these experimental conditions a good-quality biodiesel was produced, which comply with the free and total glycerol requirements of the standard UNE EN 14214 [12], even though thermal decomposition products of fatty acid methyl esters were formed; in addition, gaseous products were not generated during the process [12].

Some of the byproducts generated from glycerol during the severe supercritical process, specifically glycerol-derived ethers such as glycerol tertiary butyl ether, which is soluble in biodiesel fuels [19], affect positively the quality of the final product, reducing the viscosity and the cold flow properties of biodiesel [7,16,17]. Various ethers, such as 3-methoxy-1,2-propanediol, dimethoxymethane, 2,2-dimethoxypropane and 3-ethoxy-1,2-propanediol, obtained by reacting glycerol and methanol at 270 °C/10 MPa can be used as oxygenated additives in diesel fuel to reduce soot formation in diesel engine [20,21]. The decomposition products of fatty acid methyl esters, such as smaller-molecular-weight methyl esters, also improve the viscosity and the cold flow properties of biodiesel [15] and, therefore, a certain degree of decomposition of the unsaturated fatty acid chains could be perfectly tolerable. Other important properties of biodiesel could be affected somewhat negatively, such as the cetane number, which could decrease slightly due to decomposition of the polyunsaturated fatty acid methyl esters into smaller and more stable esters [18]. Moreover, no negative impact on the flash point was evidenced, which value decreased slightly, while the acid value increased [18]. In any case, the values of most of the properties of the biofuels produced in severe supercritical conditions were within the international biodiesel standards. This situation on biodiesel fuel quality must be assessed through a complete ASTM test, including engine performance and emission tests, which at present has not been performed yet.

The design of a new industrial supercritical transesterification technology associated with power cogeneration was developed by Deshpande et al. [22] based on the above mentioned reaction conditions. This technology consists of an one-step process without complex separation/purification steps since (i) the byproducts generated from glycerol, which remain blended within the biodiesel fuel, no longer have to be separated from the biodiesel, and (ii) all of the used alcohol reacts (a low excess of alcohol was used), eliminating the need for alcohol separation and recycling at significant pumping costs.

Glycerol decomposition and glycerol methanolysis also occurred at 270–280 °C [13,14]. Moreover, during the reaction between glycerol and supercritical methanol at 270 °C, methyl palmitate and methyl oleate were also generated [14], indicating the formation of carboxylic acids that further reacted with methanol to form the methyl esters. Decomposition products such as acetic acid from glycerol [13] have been postulated to provide necessary carboxylic acids for the methyl ester formation.

In our previous studies we investigated the evolution of both saturated and unsaturated fatty acid methyl esters [23] and the degree of thermal decomposition of fatty acid chains [24] during the supercritical methanol synthesis of biodiesel from refined soybean oil using only a methanol-to-oil molar ratio (43:1). The process was performed in a batch reactor at reaction temperatures and times ranging from 250 °C (12 MPa) to 350 °C (43 MPa) and from 15 min to 90 min, respectively. The main results obtained showed that: (i) polyunsaturated fatty acid methyl esters containing two or more double bonds (methyl linoleate and linolenate), which were generated during the reaction, partially decompose when the reaction is carried out above 300 °C, (ii) monounsaturated and saturated fatty acid methyl esters (methyl oleate and palmitate) do not decompose in the experimental conditions tested, and (iii) thermal decomposition products are detected as a broad single chromatographic peak (retention time of 20.5–23.3 min) during the analysis of supercritical reaction samples according to the standard UNE-EN 14105:2003, which is typically the norm used to determine the content of glycerides (mono-, di- and tri-glycerides) and glycerin; this new peak is composed of many overlapping peaks.

Only very few researchers have studied the effect of the alcohol-to-oil molar ratio on the degree of thermal decomposition of fatty acid chains, ethanol being used usually [25]. However, the influence of the molar ratio on the thermal decomposition during the supercritical methanol transesterification has not been studied yet. In this work, we examine the influence of the methanol-to-oil molar ratio (13:1 to 53:1) on both the thermal decomposition of fatty acid chains and the evolution of the main fatty acid methyl esters generated during the synthesis of biodiesel from soybean oil in supercritical methanol in a batch shaken tank reactor. In addition, the influence of the reaction temperature (250–350 °C) and time (15–90 min) will be studied for each methanol-to-oil molar ratio used. Furthermore, the area of the above mentioned chromatographic peak, which corresponds to the thermal decomposition products, will be used to try to predict quantitatively the degree of thermal decomposition of fatty acid chains.

2. Materials and methods

2.1. Materials

A commercial refined soybean oil, supplied by Lesieur Cristal (Roche Noires, Casablanca, Morocco), was used for this study. The fatty acid composition of the oil used, expressed in mol%, was: palmitic acid (C16:0), 11.1; estearic acid (C18:0), 3.7; oleic acid (C18:1), 24.4; linoleic acid (C18:2), 53.1; linolenic acid (C18:3), 7.2; other acids, 0.5. Anhydrous methanol was supplied by Panreac Química, S.A.U. (Castellar del Vallès, Barcelona, Spain), while methyl heptadecanoate, 1,2,4-butanetriol and 1,2,3-tricaproylglycerol (tricaprin) were supplied by Sigma–Aldrich (Tres Cantos, Madrid, Spain) and used as standards.

2.2. Experimental method

The reaction was carried out in a shaken batch tank reactor (a stainless steel cylindrical autoclave of 83 ml capacity) to investigate the influence of the reaction temperature (250–350 °C), reaction time (15–90 min) and methanol-to-oil molar ratio (13:1 to 53:1), which are the variables that most influence the synthesis of biodiesel using supercritical methanol. In each of the experiments, the reactor was loaded with 45–60 g of a methanol–soybean oil mixture, depending on the methanol-to-oil molar ratio and temperature used, and introduced pneumatically by a mechanical arm into a smelted salt bath, which permits the reaction mixture to reach the desired temperature in about 10 min. In all the experiments, the reaction time was measured from the moment the reactor was immersed in the salt bath. The reactor was continuously shaken orbitally (70 rpm) during the reaction, and, after removal from the salt bath, it was introduced in a water bath to stop the reaction; the time necessary to cool the reactor (to 90 and 45 °C) was short (around 90 and 150 s, respectively). The product obtained was evaporated by rotavapor to remove the remaining methanol and stored in a refrigerator before analysis.

2.3. Analytical methods

To determine the individual fatty acid methyl esters the standard UNE-EN 14103:2003 was applied as previously described [24]. Analyses were performed in duplicate and the error in the determination of the yield of fatty acid methyl esters was ±2.6%.

Moreover, the standard UNE-EN 14105:2003, which is normally used to analyze glycerides (mono-, di-, and tri-glycerides) and glycerol, was used in this case to determine the area of the new chromatographic peak detected (see our previous work [23]) corresponding to the thermal degradation products.

2.3.1. Determination of thermal decomposition degree of fatty acid chains

Samples were treated with BF_3/MeOH according to the AOCS Official Method Ce 2–66 in order to derivatize glycerides (mono-, di-, and tri-glycerides) and free fatty acids to the corresponding methyl esters, which were then analyzed by GC/FID, as described above. In calculating the decomposition degree, it was assumed that palmitic acid chains were resistant to degradation [23]. The decomposition degree (D), expressed as a percentage, was calculated according to the following equation, as described by Vieitez et al. [26]:

$$D = 100 \times \left[1 - \left(\frac{\sum P_i}{P_{16:0}}\right)_s \times \left(\frac{P_{16:0}}{\sum P_i}\right)_o\right]$$

where ΣP_i is the summation of the wt% of all fatty acid methyl esters, $P_{16:0}$ is the wt% of 16:0 methyl ester, and subscripts “s” and “o” indicate that the expressions between parentheses were evaluated taking into consideration the composition of the whole product and of the original oil, respectively.

3. Results and discussion

During the synthesis of biodiesel from soybean oil using supercritical methanol in batch and tubular reactors, it has been observed that thermal decomposition of fatty acid chains occurs under certain reaction conditions [5,23,24]. The degree of thermal decomposition of fatty acid chains has been quantified by many authors [11] in different reaction conditions using the method described by Vieitez et al. [26].

The pressure reached in the reactor during experiments was 10–12 MPa at 250 °C; 16–18 MPa at 275 °C; 23–26 MPa at 300 °C; 30–35 MPa at 325 °C and 36–41 MPa at 350 °C. The actual pressure in the reactor, within the pressure ranges indicated, depended on the methanol-to-oil molar ratio used; moreover, within these ranges, the effect of the pressure on the supercritical reaction was slight [5]. Therefore, all the assays were performed at pressures higher than the critical pressure of methanol (8.09 MPa).

Fig. 1 shows the degree of thermal decomposition of fatty acid chains (as a function of reaction temperature and time) for five methanol-to-oil molar ratios. As can be observed, no thermal decomposition was evident at 250 and 275 °C, regardless of the methanol-to-oil molar ratio and reaction time used. For practically all the molar ratios tested, thermal decomposition of fatty acid chains started at 300 °C when the reaction time was longer than 60 min, whilst at 325 and 350 °C it was observed from practically the outset of the reaction (15 min). Moreover, the higher the reaction temperature and the longer the reaction time used, the greater the degree of thermal decomposition observed. Therefore, the highest degree of thermal decomposition was reached at 350 °C after 90 min of reaction for all the methanol-to-oil molar ratios tested, maximum values of 40.1, 36.3, 35.5, 28.2 and 27.2% being obtained in these conditions for methanol-to-oil molar ratios of 13:1, 23:1, 33:1, 43:1 and 53:1, respectively. Similar results were reported by Vieitez et al. [26,28] during the transesterification of soybean oil using supercritical ethanol in a tubular reactor at a molar ratio of 40:1.

Table 1 shows the obtained yields of palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2) and linolenic (C18:2) acid methyl esters, and the degree of thermal decomposition. The yield of all the fatty acid methyl esters is expressed as the third part of the moles of the compound generated with respect to the moles of the initial triglycerides. It can be observed that, independently of the temperature and reaction time applied, the yield of all the fatty acid methyl esters increased with the methanol-to-oil molar ratio, indicating that the higher the methanol-to-oil molar ratio, the greater the formation of both saturated and unsaturated fatty acid methyl esters. Moreover, regardless of the methanol-to-oil molar ratio used, the yield of the saturated methyl esters and methyl oleate increased with the reaction time and temperature. In addition, the maximum yields of methyl palmitate, stearate and oleate, which were reached at 350 °C and 90 min (the most severe reaction conditions) and a methanol-to-oil molar ratio of 53:1, were very close to the contents of palmitic, stearic and oleic acid type fatty chains in the oil, respectively, indicating that these kinds of fatty acid chains were not decomposed in the experimental conditions used. However, the yields of methyl linoleate and linolenate, which increased with reaction time at temperatures lower than 300 °C, regardless of the methanol-to-oil molar ratio used, decreased between 45 and 90 min at 325 and 350 °C and were always lower than the content of linoleic and linolenic acid-type fatty chains in the oil, respectively, clearly pointing to the thermal decomposition of these two polyunsaturated fatty acid methyl esters. Hence, only polyunsaturated fatty acid methyl esters generated during the supercritical reaction suffered thermal decomposition in the experimental conditions used, and the degree of thermal decomposition observed corresponded exclusively to the disappearance of the linoleic and linolenic acid-type fatty acid chains, as was also reported in our previous work [23]. Moreover, the decrease in the polyunsaturated methyl ester yields observed between 45 and 90 min was higher at 350 °C, indicating that the thermal decomposition reactions became more intense as the temperature applied was increased, as can also be observed in Fig. 1 for all the molar ratios tested.

It can also be appreciated from Table 1 that for a 90 min reaction time at 300 °C, and for a 15 min reaction time at 325 and 350 °C, the degree of thermal decomposition remained practically unchanged, reaching values of 4.0–5.0, 3.6–4.9 and 9.8–11.9%, respectively, regardless of the methanol-to-oil molar ratio applied. However, at 325 and 350 °C, and 45 and 90 min reaction time the degree of thermal decomposition decreased with increasing molar ratios; as can be appreciated in Fig. 1, the same behavior was also observed at 60 and 75 min, the percentage values for molar ratios of 13:1, 23:1, 33:1, 43:1 and 53:1 being, respectively, 13.6, 12.9, 12.2, 9.4 and 9.2 at 60 min and 325 °C; 15.8, 15.6, 14.5, 12.4 and 12.1 at 75 min and 325 °C; 33.5, 29.8, 27.4, 23.4 and 21.5 at 60 min and 350 °C; 37.5, 31.8, 31.6, 25.7 and 25.5 at 75 min and

Table 1
Yield of the main fatty acid methyl esters and degree of thermal decomposition obtained in different supercritical reaction conditions.

T (°C)	MR	*t* (min)	Yield (mol%)					DTD (wt%)
			C16:0	C18:0	C18:1	C18:2	C18:3	
250	13:1	15	0.3	0.1	0.4	1.1	0.1	0.0
		45	1.5	0.6	3.7	6.9	1.2	0.0
		90	3.9	1.5	7.1	16.8	2.3	0.0
	23:1	15	0.3	0.1	0.7	1.4	0.2	0.0
		45	1.6	0.7	3.7	7.1	1.5	0.0
		90	4.4	1.8	8.5	20.7	3.0	0.0
	33:1	15	0.5	0.1	0.9	2.0	0.4	0.0
		45	1.8	0.8	3.8	9.4	1.7	0.0
		90	5.0	1.9	9.4	22.3	3.1	0.0
	43:1	15	0.7	0.1	0.7	2.8	0.3	0.0
		45	2.2	0.8	4.8	11.7	1.7	0.0
		90	5.2	1.7	9.7	23.1	3.3	0.0
	53:1	15	0.9	0.4	1.8	3.7	0.4	0.0
		45	3.2	1.2	5.6	13.2	1.8	0.0
		90	5.5	2.2	10.5	24.9	3.5	0.0
275	13:1	15	1.0	0.3	1.9	4.6	0.6	0.0
		45	3.3	1.6	8.1	17.0	2.4	0.0
		90	6.6	2.9	14.0	31.2	4.0	0.0
	23:1	15	1.0	0.3	1.8	5.0	0.6	0.0
		45	3.5	1.5	8.3	17.3	2.7	0.0
		90	6.7	2.8	14.4	32.8	4.0	0.0
	33:1	15	1.1	0.3	2.4	5.7	0.7	0.0
		45	4.0	1.7	8.5	18.1	2.6	0.0
		90	7.3	3.0	14.4	33.9	4.5	0.0
	43:1	15	0.9	0.3	3.1	6.5	0.6	0.0
		45	4.5	1.8	8.4	18.3	2.7	0.0
		90	7.3	2.9	14.6	34.4	4.4	0.0
	53:1	15	1.6	0.8	3.5	8.4	1.1	0.0
		45	5.0	1.9	9.1	21.5	2.8	0.0
		90	7.9	3.2	14.6	34.4	4.4	0.0
300	13:1	15	1.0	0.7	3.9	8.0	1.0	0.0
		45	5.0	2.5	13.4	26.1	3.2	0.0
		90	8.2	3.2	17.1	38.5	4.2	4.5
	23:1	15	1.4	0.8	4.2	8.2	1.1	0.0
		45	5.6	2.5	13.3	27.2	3.4	0.0
		90	8.3	3.5	17.1	38.8	4.3	4.0
	33:1	15	1.8	0.7	4.4	9.7	1.2	0.0
		45	6.4	2.6	13.6	29.0	3.6	0.0
		90	8.9	3.6	17.4	40.5	4.5	5.0
	43:1	15	1.9	0.9	5.1	10.9	1.3	0.0
		45	6.7	2.7	14.1	32.2	3.7	0.0
		90	8.7	3.6	17.6	40.6	4.7	4.2
	53:1	15	2.8	1.2	5.6	13.2	1.7	0.0
		45	6.9	2.7	14.6	33.2	3.8	0.0
		90	9.0	3.7	17.8	41.3	4.9	5.0
325	13:1	15	3.7	1.9	9.0	22.0	2.5	3.6
		45	7.2	3.5	17.4	34.3	3.7	9.8
		90	9.3	3.5	19.5	33.0	4.0	20.0
	23:1	15	3.7	1.8	9.5	22.1	2.5	4.6
		45	7.1	3.4	18.3	35.0	3.7	9.1
		90	9.3	3.6	20.7	34.3	4.0	18.3
	33:1	15	3.8	1.9	9.9	22.3	2.6	3.9
		45	7.2	3.4	18.5	37.6	4.0	8.2
		90	9.4	3.5	20.3	35.7	4.0	17.8
	43:1	15	4.1	2.0	9.9	22.7	2.6	4.4
		45	7.7	3.5	19.0	38.1	3.9	7.4
		90	9.5	3.8	20.7	36.2	4.0	16.0
	53:1	15	5.8	2.2	10.6	23.7	2.7	4.9
		45	9.8	3.8	19.4	39.4	4.0	7.0
		90	10.4	4.4	20.7	37.2	4.0	14.6
350	13:1	15	6.7	2.5	13.8	19.9	2.5	9.8
		45	9.7	3.3	21.2	24.7	4.7	29.7
		90	9.6	4.3	23.3	11.1	3.9	40.1
	23:1	15	7.2	3.2	13.8	20.3	2.6	11.0
		45	9.9	3.5	22.5	24.5	5.0	22.9
		90	9.7	4.5	22.8	12.1	4.0	36.3
	33:1	15	7.5	3.2	16.2	23.4	3.0	11.6
		45	10.1	3.9	23.1	26.5	4.9	22.3
		90	9.9	4.7	24.7	15.8	4.2	35.5

Table 1 (*Continued*)

T (°C)	MR	*t* (min)	Yield (mol%)					DTD (wt%)
			C16:0	C18:0	C18:1	C18:2	C18:3	
	43:1	15	7.7	3.7	18.1	27.4	3.1	9.9
		45	10.7	4.5	23.1	27.3	4.8	18.5
		90	10.8	4.7	24.7	16.7	4.1	28.2
	53:1	15	9.5	3.7	18.3	28.8	3.4	11.9
		45	12.3	4.6	23.8	27.6	4.9	17.2
		90	12.1	4.7	24.5	17.8	4.1	27.2

T, reaction temperature; MR, methanol-to-oil molar ratio; *t*, reaction time; DTD, degree of thermal decomposition.

350 °C. Moreover, the decrease in thermal decomposition with increasing methanol-to-oil molar ratios at temperatures higher than 300 °C and reaction times longer than 45 min coincides with the increase in yield of the polyunsaturated fatty acid methyl esters, indicating that the methanol-to oil molar ratio favors the synthesis of biodiesel because it has a certain protective effect against the thermal decomposition of the polyunsaturated fatty acid methyl esters.

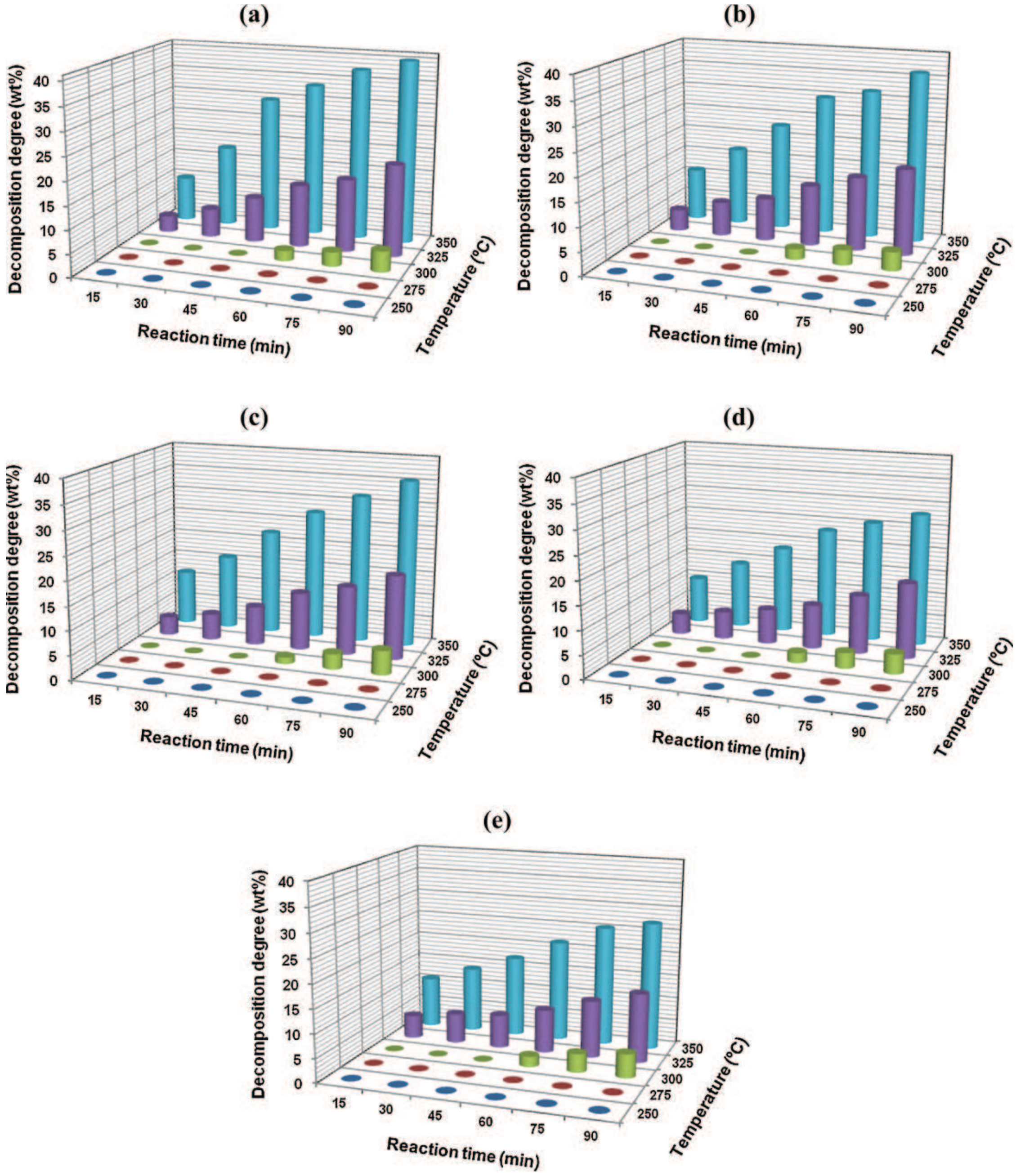

Fig. 1. Degree of thermal decomposition as a function of reaction temperature and time for methanol-to-oil molar ratios of (a) 13:1, (b) 23:1, (c) 33:1, (d) 43:1, and (e) 53:1.

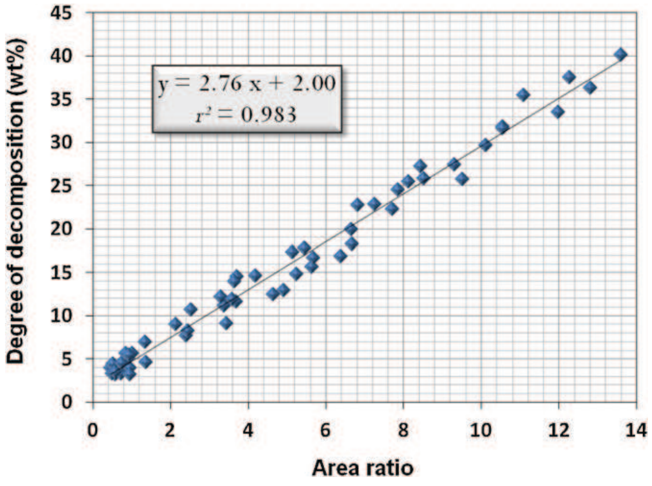

Fig. 2. Relationship between the degree of thermal decomposition and the area ratio between the peak corresponding to the thermal decomposition products and that of tricaprin (internal standard).

During the synthesis of biodiesel from soybean oil using supercritical ethanol in a microtube reactor [25,27], thermal decomposition was lower than 5%, regardless of the reaction conditions used (up to 325 °C, a residence time of 45 min and a 40:1 molar ratio). These degrees of decomposition were slightly lower than those obtained in our study in a batch reactor, probably because the processes of mass transfer were more intense in the microtube reactor as a consequence of a greater specific surface area. Moreover, the same authors observed a decrease in the decomposition of fatty acid chains with increasing ethanol-to-oil molar ratios, which agrees with the results obtained in our study.

Vieitez et al. [26] obtained degrees of decomposition of 6, 16 and 26% at 300, 325 and 350 °C, respectively, during the synthesis of biodiesel from soybean oil using supercritical ethanol in a tubular reactor with an ethanol-to-oil molar ratio of 40:1, a flow rate of 0.8 ml/min and a pressure of 20 MPa. These results agree with those reported in our study (4.2, 16 and 28.2% at 300, 325 and 350 °C, respectively) for a reaction time of 90 min and a methanol-to-oil molar ratio of 43:1. Vieitez et al. [28] also obtained similar results during the supercritical methanolysis of soybean oil in a tubular reactor.

As previously reported [23], during the chromatographic analysis of supercritical reaction samples according to the standard UNE-EN 14105:2003, an unexpected peak (composed of the thermal degradation products generated during the supercritical methanol reaction) was detected in certain reaction conditions (see chromatograms in Fig. 1 in our previous work [23]). In order to examine the relation between the degree of thermal decomposition, determined according to the equation proposed by Vieitez et al. [26] after treatment of the samples by the AOCS official method Ce 2–66, and the ratio between the area of this new chromatographic peak detected and that of tricaprin (internal standard used by the norm UNE-EN 14105:2003), a simple linear regression analysis was performed. Some difficulty was experienced in accurately determining the area of the first mentioned peak when the degree of decomposition was low (between 3 and 6%) because the peak overlapped some of those corresponding to the diglycerides remaining in the medium; however, in most cases where the reaction conditions led to higher degrees of thermal decomposition, diglycerides were hardly detected in the medium as they disappeared quickly when the treatment severity increased.

Fig. 2 shows the degree of thermal decomposition versus the area ratio between the two above mentioned chromatographic peaks for 55 experiments carried out in different reaction conditions (300–350 °C, 15–90 min and 13:1 to 53:1 methanol-to-oil molar ratio). As can be appreciated, the points tend toward a straight line. Therefore, the fitting of the data in Fig. 2 to a simple linear regression model produced a least-squares regression line ($Y = 2.0002 + 2.7604X$, where Y represents the degree of thermal decomposition, expressed in wt%, and X represents the area ratio between the two chromatographic peaks) with a correlation coefficient r of 0.9911, a coefficient of determination r^2 of 0.9831, an adjusted r^2 coefficient of 0.9827 and a standard error of 1.3838. Hence, taking into account the good fit of the data to this simple linear regression model, the degree of thermal decomposition of the fatty acid chains can be suitably predicted in a simple manner from the area ratio between the peak corresponding to the thermal decomposition products (the new peak detected) and the peak corresponding to tricaprin. Therefore, the standard UNE-EN 14105:2003 can also be used directly to quantify the degree of thermal decomposition of fatty acid chains during the synthesis of biodiesel using supercritical methanol from refined soybean oil.

4. Conclusions

The results obtained in this study suggest that the synthesis of biodiesel using supercritical methanol in a batch reactor should be performed at temperatures below 300 °C to avoid the thermal decomposition of the fatty acid chains. The use of higher temperatures might cause significant decomposition reactions in the lipid material, especially of the polyunsaturated fatty acid chains, leading to a decrease in the biodiesel yield. The results also show that the methanol-to-oil molar ratio used not only favored the formation of all the fatty acid methyl esters, but also had a certain protective effect against the thermal decomposition of the polyunsaturated ones. Further studies should be performed to investigate whether the use of additives could prevent the development of decomposition reactions of the polyunsaturated fatty acid chains during the supercritical process. Furthermore, it has been demonstrated that the area of a new chromatographic peak (which corresponded to the thermal decomposition products) detected during the analysis of the reaction samples according to the standard UNE-EN 14105:2003 can be used to quantify the degree of thermal decomposition of the fatty acid chains.

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References

[1] T. Pinnarat, P.E. Savage, Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions, Industrial and Engineering Chemistry Research 47 (2008) 6801–6808.
[2] E.S. Song, J.W. Lim, H.S. Lee, Y.W. Lee, Transesterification of RBD palm oil using supercritical methanol, J. Supercritical Fluids 44 (2008) 356–363.
[3] S. Saka, D. Kusdiana, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel 80 (2001) 225–231.
[4] D. Kusdiana, S. Saka, Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol, J. Chemical Engineering of Japan 34 (2001) 383–387.
[5] H. He, T. Wang, S. Zhu, Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process, Fuel 86 (2007) 442–447.
[6] H.Y. Shin, S.M. Lim, S.Y. Bae, S.C. Oh, Thermal decomposition and stability of fatty acid methyl esters in supercritical methanol, J. Analytical and Applied Pyrolysis 92 (2011) 332–338.
[7] H. Imahara, E. Minami, S. Hari, S. Saka, Thermal stability of biodiesel in supercritical methanol, Fuel 87 (2008) 1–6.
[8] N.M. Niza, et al., Biodiesel production by non-catalytic supercritical methyl acetate: thermal stability study, Applied Energy (2012), http://dx.doi.org/10.1016/j.apenergy.2012.03.033.

[9] M.M. Conceiçao, V.J. Fernandes, A.S. Araújo, M.F. Farias, I.M.G. Santos, A.G. Souza, Thermal and oxidative degradation of castor oil biodiesel, Energy and Fuels 21 (2007) 1522–1527.
[10] I.S. Patrikios, P.C. Patsalis, Monounsaturated fatty acid oligomerization is responsible for the agglutination activity of heated virgin olive oil, Food Research International 36 (2003) 985–990.
[11] I. Vieitez, C. Silva, I. Alckmin, F. Castilhos, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Stability of ethyl esters from soybean oil exposed to high temperaturas in supercritical ethanol, J. Supercritical Fluids 56 (2011) 265–270.
[12] V.F. Marulanda, G. Anitescu, L.L. Tavlarides, Biodiesel fuels through a continuous flow process of chicken fat supercritical transesterification, Energy and Fuels 24 (2010) 253–260.
[13] N. Aimaretti, D.L. Manuale, V.M. Mazzieri, C.R. Vera, J.C. Yori, Batch study of glycerol decomposition in one-stage supercritical production of biodiesel, Energy and Fuels 23 (2009) 1076–1080.
[14] S. Lee, D. Posarac, N. Ellis, An experimental investigation of biodiesel synthesis from waste canola oil using supercritical methanol, Fuel 91 (2012) 229–237.
[15] W. Iijima, Y. Kobayashi, K. Takekura, K. Taniwaki, The non-glycerol process of biodiesel fuel treated in supercritical methanol, in: Presented at the 2004 ASAE/CSAE Annual International Meeting, Ottawa, ON, Canada, 2004, Paper No. 046073.
[16] G. Anitescu, A. Deshpande, L.L. Tavlarides, Integrated technology for supercritical biodiesel production and power cogeneration, Energy and Fuels 22 (2008) 1391–1399.
[17] V.F. Marulanda, G. Anitescu, L.L. Tavlarides, Investigations on supercritical transesterification of chicken fat for biodiesel production from low-cost lipid feedstocks, J. Supercritical Fluids 54 (2010) 53–60.
[18] R. Sawangkeaw, S. Teeravitud, K. Bunyakiat, S. Ngamprasertsith, Biofuel production from palm oil with supercritical alcohols: effects of the alcohol to oil molar ratios on the biofuel chemical composition and properties, Bioresource Technology 102 (2011) 10704–10710.
[19] H. Noureddini, W.R. Dailey, B.A. Hunt, Production of ethers of glycerol from crude glycerol – the by-product of biodiesel production, in: Chemical and Biomolecular Engineering Research and Publications, Papers in Biomaterials, University of Nebraska-Lincoln, Lincoln, NE, 1998, pp. 1–14.
[20] M. Ikura, Conversion of glycerol to naphtha-range oxygenates, US Patent 20100016641 (2010) A1.
[21] P. Pepiot-Desjardins, H. Pitsch, R. Malhotra, S. Kirby, A. Boehman, Structural group analysis for soot reduction tendency of oxygenated fuels, Combustion and Flame 154 (2008) 191–205.
[22] A. Deshpande, G. Anitescu, P.A. Rice, L.L. Tavlarides, Supercritical biodiesel production and power cogeneration: technical and economic feasibilities, Bioresource Technology 101 (2010) 1834–1843.
[23] J. Quesada-Medina, P. Olivares-Carrillo, Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol, J. Supercritical Fluids 56 (2011) 56–63.
[24] P. Olivares-Carrillo, J. Quesada-Medina, Synthesis of biodiesel from soybean oil using supercritical methanol in a one-step catalyst-free process in batch reactor, J. Supercritical Fluids 58 (2011) 378–384.
[25] C. Silva, F. Castilhos, J.V. Oliveira, L.C. Filho, Continuous production of soybean biodiesel with compressed ethanol in a microtube reactor, Fuel Processing Technology 91 (2010) 1274–1281.
[26] I. Vieitez, C. Silva, I. Alckmin, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Effect of temperature on the continuous synthesis of soybean esters under supercritical ethanol, Energy and Fuels 23 (2009) 558–563.
[27] C. Silva, A.P. Lima, F. Castilhos, L.C. Filho, J.V. Oliveira, Non-catalytic production of fatty acid ethyl esters from soybean oil with supercritical ethanol in a two-step process using a microtube reactor, Biomass and Bioenergy 35 (2011) 526–532.
[28] I. Vieitez, C. Silva, I. Alckmin, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Continuous catalyst-free methanolysis and ethanolysis of soybean oil under supercritical alcohol/water mixtures, Renewable Energy 35 (2010) 1976–1981.

VIII. Índices de calidad de las publicaciones

Índices de calidad de las publicaciones

Artículo 1: **Supercritical Biodiesel Production from Raw Soybean Oil.**

Quesada, J.; Olivares, P.
***Journal of Biofuels*, 1 (2010) 115-122.**

Indexada en Index Copernicus International.

I C Journals Master List (2011): **4.88**

Número de citas: ninguna hasta el momento.

Artículo 2: **Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol.**

Quesada-Medina, J.; Olivares-Carrillo, P.
***Journal of Supercritical Fluids*, 56 (2011) 56-63.**

Factor de Impacto (2011): **2.860**

Posición: **17/133**, 1er cuartil de la categoría **Chemical Engineering** del Journal Citation Reports, JCR.

Número de citas: **7** en artículos de revistas de alto factor de impacto tales como *Bioresource Technology, Energy and Fuels, Journal of Cleaner Production, Fuel Processing Technology, Journal of Supercritical Fluids* y *Journal of Analytical and Applied Pyrolysis.*

Artículo 3: **Synthesis of biodiesel from soybean oil using supercritical methanol in a one-step catalyst-free process in batch reactor.**

Olivares-Carrillo, P.; Quesada-Medina, J.
***Journal of Supercritical Fluids*, 58 (2011) 378-384.**

Factor de Impacto (2011): **2.860**

Posición: **17/133**, 1er cuartil de la categoría **Chemical Engineering** del Journal Citation Reports, JCR.

Número de citas: **5** en artículos de revistas de alto factor de impacto tales como *Fuel*, *Industrial and Engineering Chemistry Research* y *Journal of Supercritical Fluids*.

Artículo 4: **Thermal decomposition of fatty acid chains during the supercritical methanol transesterification of soybean oil to biodiesel.**

Olivares-Carrillo, P.; Quesada-Medina, J.
***Journal of Supercritical Fluids*, 72 (2012) 52-58.**

Factor de Impacto (2011): **2.860**

Posición: **17/133**, 1er cuartil de la categoría **Chemical Engineering** del Journal Citation Reports, JCR.

Número de citas: ninguna hasta el momento.