(54) Title: PROCESS FOR MANUFACTURING ACID ESTERS THROUGH REACTIVE DISTILLATION
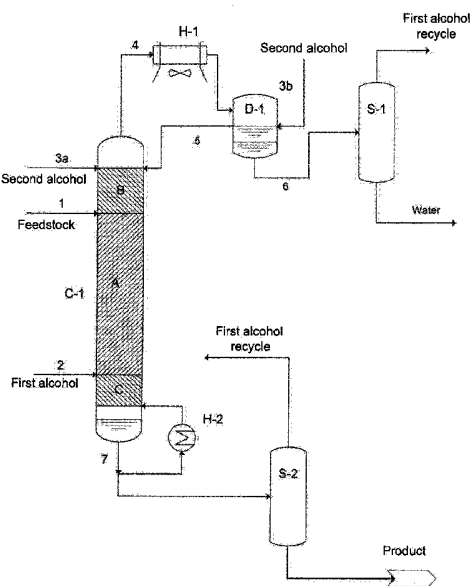
Figure 1

(57) Abstract: The present invention pertains to a process for the manufac-
ture of acid esters through reactive distillation, wherein a carboxylic acid is
submitted to esterification in a reaction section of a reactive distillation
column with an alcohol in the presence of a solid acid catalyst to form an
acid ester, wherein a first supply stream comprising the carboxylic acid, a
second supply stream comprising a first alcohol and a third supply stream
comprising a second alcohol, the second alcohol having a higher molecular
weight than the first alcohol, are supplied to the reactive distillation col-
umn, therein the first supply stream is supplied to the column at a first en-
try level located just above or at the top of the reaction section, the second
supply stream is supplied to the column at a second entry level located in
or just below the reaction section and below the first entry level, and the
third supply stream is supplied to the column at a third entry level located
above the first entry level, and wherein a bottom stream comprising the es-
ter formed is obtained and a top stream comprising unreacted first alcohol,
water and unreacted second alcohol is obtained. The process is particularly
suitable for the manufacture of biodiesel from a fatty acid rich feedstock, in
particular a feedstock which comprises C10-C18 fatty acids and triglyc-
erides of C10-C18 fatty acid.

Process for manufacturing acid esters through reactive distillation

The present invention pertains to a process for manufacturing acid esters through reactive distillation. The process is particularly suitable for the manufacture of biodiesel from waste lipid materials by employing a solid

5   catalyst in a reactive distillation process. In one embodiment a multi-segment tubular liquid-phase reactor is used in combination with a reactive distillation unit.

Biodiesel is a sustainable and renewable fuel pro-

10   duced from various oils, fats and free fatty acids. Conventional feedstock include vegetable and animal lipid materials, more specifically frying and cooking fats (henceforth referred to as "waste fats"), vegetable edible and non-edible oils, animal fats from food processing, indus-

15   trial greases and solvents, tall oil resulting from kraft pulping and other new renewable sources, such as oil from algae.
       These materials are reacted with alkyl alcohols.
The resulting product is a mixture of fatty acid esters whose

20   application properties as fuel is similar to the conventional petrodiesel fuel obtained from petroleum. Today for the most part the biodiesel is manufactured by the transesterification reaction of glycerides with mono-alcohols. In this reaction, one molecule of triglyceride reacts with one, two, or three

25   molecules of mono-alcohol (most commonly methanol), producing one, two, or three molecules of mono-alkyl fatty esters and water, respectively. Current biodiesel processes typically use an excess of alcohol to shift the chemical equilibrium, increase the rate of the forward reaction, and help fat solu-

30   bilisation in the liquid mixture. The transesterification is

typically catalysed by a homogeneous base catalyst. NaOH, KOH and their corresponding alkoxides are the most used, as described by B. Gutsche in Fett/Lipid 99 (12), 418 (1997). The manufacturing of biodiesel employing heterogeneous base cata-
5   lysts has been successfully implemented as described in EP-A-1 352 893, US patent 5,908,946 and US patent 6,147,196. Note that using base catalysts requires a feedstock with low free fatty acid (FFA) content, typically below 1% FFA, but preferably below 0.5% FFA, as well as low water content,
10 typically below 500 ppm. The above conditions can be met only by some edible virgin oils. Conversely, waste oil and fat contain typically between 4% FFA and 20% FFA. Consequently, a pre-esterification step is necessary, which typically uses an acid catalyst. Thus, biodiesel manufacturing from waste oil
15 or fat should employ two catalysts, an acid for the esterification pre-treatment, and a base for the transesterification stage.

        Another route to the above-mentioned mono-alkyl esters is the direct esterification of the fatty acids with
20 mono-alcohols. In this reaction, one molecule of fatty acid reacts with one molecule of alcohol, producing one molecule of mono-alkyl fatty ester and one molecule of water. This esterification is catalysed by strong acid catalysts. Current biodiesel processes typically use an excess of alcohol to
25 shift the chemical equilibrium and to increase the rate of the forward reaction. Waste oils may contain variable amounts of FFA, typically between 5% FFA and up to 100% FFA. These oils and fats are available from various sources, including waste frying oils from restaurants and industrial food proc-
30 essing, yellow grease and animal fats, as well as the tall oil obtained by paper milling. The prices of high-FFA oils are typically less than 50% than those of crop oils. Consequently, these are valuable sources for making low-cost biodiesel with the benefits of avoiding environment pollution

An alternative approach to tackle the variability of raw materials is the full hydrolysis of triglycerides to fatty acids, which can be further submitted to esterification, as described further in this invention. A suitable
5 method is sub-critical water hydrolysis that can take place at temperatures of 270 °C to 320 °C and pressures of 10 MPa to 20 MPa. The reaction time can be significantly reduced by an autocatalytic effect due to the initial FFA present in the feedstock [Minami, Saka, Fuels, 2479, 2006]. Up to 90% of the
10 triglycerides can be converted to fatty acid in one step.

The Cetane Number (CN) is an important combustion characteristic of a diesel-type fuels. A minimum CN of 49 is required by the norm DIN 14214. It is known that the CN of fatty acid methyl esters (FAME) increases with the chain
15 length, but decreases with the unsaturation in the hydrocarbon chain. The presence of fatty acid esters of long-chain alcohols, such as butanols or 2-ethyl-hexanol (2EH), increases the CN and as result the biodiesel's combustion capability, but does not affect its viscosity. For example
20 2EH fatty acid ester has a high CN (Knothe at al., Fuel 82, 971, 2003) and should improve also the cloud point (Foglia et al., J. Am. Oil. Chem. Soc. 74, 951, 1997). Hence, the fatty esters of longer chain alkyl alcohol improve the quality of biodiesel mixtures originating from highly unsaturated feed-
25 stock, as rapeseed, palm, sunflower or soybean oils. Note that 2EH is a low cost byproduct of n-butyraldehyde production.

Typically, the esterification reaction is catalysed by strong acids, such as H_2SO_4, HCl, or $p-Me(C_6H_4)SO_3H$. A fun-
30 damental disadvantage of using a homogeneous acid catalyst is that it must be neutralised, washed and removed from the product. These operations increase both the capital investment and the operational costs, require additional chemicals and generate contaminated water effluents that must submitted
35 to costly treatment. The low legal limit of sulphur impuri-

ties allowed in diesel (currently < 20 ppm) also increases separation costs when sulfur-containing homogeneous catalysts such as H_2SO_4 or p-$Me(C_6H_4)SO_3H$ are used.

Heterogeneous catalysts remain active in-situ for longer periods, do not require chemical neutralisation and do not generate harmful waste. These characteristics greatly simplify the technology. When the solid catalyst finally deactivates, it can be regenerated and reused. In general, solid acid catalysts (SAC) are preferred for esterification and solid base catalysts (SBC) for transesterification.

SAC are suitable for catalysing fatty acid esterification. Acid resins, such as Nafion and Amberlyst, exhibit good activity, but can be employed only at low to moderate temperatures, in general bellow 130 °C. Omota, Dimian and Bliek (Chem. Eng. Sci., 58, 3175, 2003) describes the use of sulphated zirconia as SAC for the esterification of fatty acids with alkyl alcohols as well as its implementation in reactive distillation based manufacturing processes. Kiss, Omota, Dimian and Rothenberg (Topics in Catalysis, Vol. 40, no.1-4, 2006) investigated the use of various solid catalysts by the esterification of dodecanoic acid with methanol, 1-propanol, and 2-ethyl hexanol.

The use of niobic acid was described recently in US patent application 2007/0232817 A1. Metal oxides can be also applied with better results, since allow using higher reaction temperatures, up to 200°C, with higher productivity and better opportunity for heat integration (Kiss, Dimian and Rothenberg, Energy and Fuels, 2008, 22,598). It is noted that the use of heterogeneous catalysts enables performing the reactions at higher temperatures, resulting also in better use of energy from the heat integration viewpoint.

All esterification reactions produce stoichiometric amounts of water. This water must be removed from the reaction vessel, to shift the chemical equilibrium to the

products side and ensure high FFA conversion. When a hetero-
geneous catalyst is used, water removal is necessary to avoid
catalyst deactivation. For example, when sulphated zirconia
comes is in contact with free water, sulphonic acid groups
5   may be leached from the catalyst (Kiss, Dimian and Rothen-
berg, Energy and Fuels, 2008, 22,598). One way to solve this
problem is by using Reactive Distillation (RD), also known as
Catalytic Distillation. Above 100°C, the water formed by the
reaction migrates from the liquid reactive phase to the va-
10   pour phase, from which it can be continuously removed by
condensation and liquid-liquid separation (Dimian, Omota and
Bliek, Chem. Eng. Sci., 59, 3175-3185 2003). When the alcohol
forms an azeotrope with water, as in the case of propanols,
this can be broken by using a suitable entrainer (Dimian,
15   Omota and Bliek , Chemical Engineering & Processing, 43, 411-
420, 2004).

      The use of an excess of alcohol increases the reac-
tion rate and ensures higher flexibility with respect to FFA
20   content in the feedstock. However, the alcohol excess must be
recovered and recycled, which in turn implies additional
equipment and separation costs. In a reactive distillation
environment a hard constraint can arise from the excessive
reboiler temperature due to very high boiling points of fatty
25   acid esters. In this case, the dilution of the bottom product
with alcohol can lower the reboiler temperature to acceptable
values. As a result, an optimisation of the alcohol excess is
necessary, that takes into account the alcohol recycle costs
while fulfilling the constraints, such as high FFA conversion
30   and adequate operating temperature.
      Since both esterification and transesterification
reactions are almost neutral with regard to heat of reaction,
biodiesel manufacturing does not involve important energy
costs due to the chemical reaction steps. The energy costs
35   are mainly due to physical separation processes. Therefore,

reducing the number of separation steps (which are mainly wa-
ter washing and distillation), results in substantial
savings. This can be done using heterogeneous catalysts.

5   Reactive distillation is a suitable technique for
biodiesel manufacturing. A reactive distillation column has
three zones: a reaction zone where the chemical reactions
producing biodiesel take place, and two separation zones, one
separation zone at the top, for water removal and alcohol re-
10   cycling, and one separation zone at the bottom for alcohol
separation from fatty ester product. In the case of esterifi-
cation the key advantage is that the water produced by
reaction can be removed continuously from the liquid to the
vapour phase by operating the unit at sufficiently high tem-
15   peratures, in general above 100°C, as discussed above. In the
case of transesterification of a feedstock containing
triglycerides, the key advantage to the use of a reactive
distillation process is the possibility of generating a much
larger ratio alcohol/triglyceride than is needed by
20   stoichiometry, which is necessary to ensure homogeneous liq-
uid reaction phase, higher driving force and control of
temperature profile.

        The problem underlying the present invention is the
25   provision of a reactive distillation process, in particular a
reactive distillation process for the manufacture of bio-
diesel, which can be operated under more economic conditions,
and which provides a product with better properties as com-
pared to reactive distillation processes described in the
30   art.

        The present invention is directed to a process for
the manufacture of carboxylic acid esters through reactive
distillation, wherein a carboxylic acid is reacted in a reac-
35   tion section of a reactive distillation column with an

alcohol under esterification conditions in the presence of a
catalyst to form an ester, wherein a first supply stream com-
prising the carboxylic acid, a second supply stream
comprising a first alcohol and a third supply stream compris-
5   ing a second alcohol, the second alcohol having a higher
molecular weight than the first alcohol, are supplied to the
reactive distillation column, wherein the first supply stream
is supplied to the column at a first entry level located just
above or at the top of the reaction section, the second sup-
10   ply stream is supplied to the column at a second entry level
located in or just below the reaction section and below the
first entry level, and the third supply stream is supplied to
the column at a third entry level located above the first en-
try level, and wherein a bottom stream comprising the ester
15   formed is obtained and a top stream comprising unreacted
first alcohol, unreacted second alcohol and water is ob-
tained.

The crux of the process according to the invention
20   is that it is a dual esterification process based on the use
of both a first and a second alcohol, wherein the second al-
cohol has a higher molecular weight than the first alcohol,
and the two alcohols are provided to the reactor at different
locations. The second alcohol has the combined function of
25   entrainer of water and co-reactant in the esterification and
transesterification reactions.

The process according to the invention has various
advantages as compared to the prior art processes which do
30   not use the combination of a first and a second alcohol. In
the first place, the use of the second alcohol results in the
formation of higher-alcohol fatty acid esters which have a
favourable effect on the combustion properties of the bio-
diesel, as their presence enhances the cetane number.
35   Further, by in situ water removal in the process according to

the invention, the chemical equilibrium is shifted in such a
way that high conversion of fatty acids is obtained, in gen-
eral at least 85%, preferably at least 90%, more preferably
at least 95%. In some embodiments it may be possible to ob-
5   tain a conversion of at least 97%, at least 98%, or at least
99%. These conversion percentages also apply to any triglyc-
erides present in the feedstock. Additionally, catalyst
deactivation is minimised, which leads to a more stable oper-
ating process. Further, the process can be carried out at
10   lower pressures than conventional processes. More in particu-
lar, the pressure can be decreased from 15-20 bars as used
conventionally to, in a preferred range, 2-6 bar. The excess
of light alcohol is decreased as compared to conventional
processes.
15

In one embodiment of the process according to the
invention the first alcohol is selected from methanol, etha-
nol, propanols, and mixtures thereof.

The second alcohol is preferably selected from
20   mono-alkyl-alcohols with 4 to 10 carbon atoms, in particular
6 to 8 carbon atoms.

In a preferred embodiment of the present invention
the carboxylic acid is selected from C10 to C18 fatty acids,
and mixtures thereof. These fatty acids may be derived from
25   lipid material derived from animal fats, vegetable oils, al-
gae oil or mixtures thereof, including recycled fats, oils
and solvents. The feedstock contains 1-100wt.% of fatty ac-
ids, more preferable 5 to 100 % FFA.

In one embodiment of the present invention the
30   feedstock comprises C10-C18 fatty acids in combination with
fatty acid triglycerides. The amount of fatty acid and
triglycerides in the feed varies with the source. In general,
the feedstock contains 1-100wt.% of fatty acids. In one em-
bodiment, where the feedstock is derived from oil and non-
35   waste fats, the feedstock contains between 1-30 wt.% of C10-

C18 fatty acids and 99-70 wt.% of triglycerides of C10-C18
fatty acids. In another embodiment, where the feed is derived
from waste fats, the feed generally contains 5-100% of C10-
C18 fatty acids and 0-95 wt.% of triglycerides of C10-C18
5   fatty acids.

The present invention will be elucidated by way of
reference to the figure 1.

In the drawing the reactive distillation column (C-
10   1) comprises a reaction section (A), a separation section (B)
and a bottom separation section (C).

A first supply stream comprising the carboxylic
acid feedstock, e.g., the FFA feedstock, is fed to the column
through a line (1) which enters the column at a first entry
15   level located above or at the top of the reaction section
(A).

A second supply stream comprising the first alcohol
is fed to the column through a line (2) which enters the col-
umn at a second entry level located just below reaction
20   section (A) or directly in the reboiler of the column. As il-
lustrated in figure 1, the second alcohol can be fed to the
top of the column (C-1) above the separation section (B)
through the line (3a).

A top vapor stream is withdrawn from the top of the
25   reactor through line (4). This top stream comprises unreacted
first alcohol, unreacted second alcohol, and water. After
condensation in the heat exchanger (H-1), which may be air-
cooled or water-cooled, the resulting mixture is submitted to
a liquid-liquid separation in the decanting vessel (D-1). It
30   results an organic phase containing first and second alco-
hols, and an aqueous fraction containing water and sometimes
first alcohol. The organic phase is refluxed to the reactive
distillation column as the stream (5) to an entry point at
the top, or slightly above, the separation section (B). The
35   aqueous phase from the decanter (D-1) is fed through line (6)

to a further separation unit (S-1), where first alcohol is
separated from water and recycled to the reactive distilla-
tion column (C-1). In a preferred embodiment the second
alcohol is fed directly into the flash drum (D-1) on level
control via the line (3b) entering the column together with
the organic phase reflux (6) from the decanter (D-1)) de-
scribed above. It has been found that this make-up policy
allows more robust operation by adapting dynamically the
amount of the second alcohol to the consumption by the es-
terification reaction as well as to the inventory necessary
as water entrainer.

The product stream withdrawn from the bottom of the
unit (C-1) through line (7) comprises the fatty acid esters,
unreacted first alcohol, traces of the second alcohol and
traces of water. This stream is subjected to a further proc-
essing in a separation unit (S-2), where first alcohol is
separated from the product. The light alcohol may be recycled
to the column. Het exchanger (H-2) provides energy input to
the unit.

The reaction section (A) comprises a solid acid
catalyst (SAC) which is effective to convert under esterifi-
cation conditions the carboxylic acid with the first alcohol
and/or the second alcohol to form the resulting esters. Exam-
ples of suitable heterogeneous strong acidic catalysts are
strong acidic ion-exchange resins as Amberlyte™ and Nafion™,
acidic ZSM-5 zeolite and acidic beta zeolite, sulphonated or
phosphonated inorganic catalysts like sulphonated zirconia or
phosphonated zirconia, niobic acid.

The solid catalyst is hosted in a fixed bed ar-
rangement. In one embodiment, the reactive zone consists of
structured packing filled with shaped catalyst particles,
e.g., catalyst particles shaped as spheres. Other particle
shapes may also be used. Examples of suitable packing are

Katapack from Sulzer, or Multipack from Monza. Suitable par-
ticle size is of 0.8 to 1.2 mm diameter.

The reactive distillation column may have from 10
to 40 equivalent reactive stages, more preferably of 20 to 30
reactive stages, while the number of stages per meter (NSM)
can be between one and five, more preferably between two and
three.

In addition to the solid acid catalyst, the reac-
tion zone A can also include a solid base catalyst, for
carrying out the transesterification reaction to the fatty
acid esters. This arrangement is of particular interest when
the feedstock contains a relatively high amount of fatty acid
triglycerides, e.g., where the feedstock contains 1-50 wt.%
of C10-C18 fatty acids and 50-99 wt.% of C10-C18 fatty acid
triglycerides, in particular 2-20 wt.% of C10-C18 fatty acids
and 80-98 wt.% of C10-C18 fatty acid triglycerides. In this
case the in-situ removal of water resulting from the esteri-
fication of free fatty acids can be exploited in the sense of
protecting de solid base catalyst against deactivation. It is
known that the feedstock submitted to transesterification by
solid base catalysts should have very low water content, in
general less than 1 wt.%, but preferably less than 500 ppm.

Suitable solid base catalysts are known in the art.
For example, hydrotalcite or other layered hydroxide com-
pounds may be used. Where a solid base catalyst is present,
it is placed in a second reaction zone below the reaction
zone containing a solid acid catalyst. This ensures the fur-
ther conversion of the triglycerides present in the lipid
feedstock to monoalkyl fatty esters. The absence of water and
fatty acids in the feedstock as it is in contact with the
base catalyst greatly helps the preservation of activity of
the solid base catalyst.

The base catalyst reactive zone may have from 5 to
30 equivalent reactive stages, more preferably of 5 to 10 re-
active stages, while the number of stages per meter (NSM) can

be between one and five, more preferably between two and three. As before, in one embodiment the reactive zone consists of structured packing filled with shaped catalyst particles.

5   The preferred shape of the particles is spheres, of 0.8 mm to 1.2 mm diameter, but other particle shapes and sizes may be used as well. Examples of suitable commercial packing formats are Katapack™ from Sulzer, or Multi-pack™ from Monza.

10   The first alcohol can be fed entirely at the bottom of the reactive zone, which comprises now both acid solid catalyst and base solid catalyst sections, or partially split to each zone according to reaction requirements.

          The reactive distillation column is operated at a
15   pressure between ambient pressure and 20 bar, preferably between 1 and 10 bar, more preferably between 3 and 6 bar. It is noted that the use of a combination of a first and second alcohol allows a significant reduction of the operating pressure required to obtain vapour-liquid equilibrium temperature
20   as compared to the case where only a first alcohol is used. For example, when methanol and 2-ethyl-hexanol are used in the esterification of oleic acid, the required pressure to obtain a temperature of 130°C is 1.5 bar. When only methanol is used, the required pressure is 8 bar.

25   The operating temperature profile satisfies vapour-liquid equilibrium condition corresponding to the composition of the reactive and non-reactive mixtures. The temperature of the reaction zone may be between 100°C and 220°C, more preferable between 130 and 170°C. The bottom temperature should
30   not exceed 200 °C. This can be controlled by allowing sufficient alcohol in the bottom product.

          In general, the preheated feedstock is fed at the top of the reactive reaction section at a temperature between 100-200 °C, more preferably between 130-180 °C.

The first alcohol can be introduced as liquid, as vapour, or as superheated vapour. In one embodiment, the first alcohol is introduced as superheated vapour at the base of the reaction zone. In other embodiment, it is introduced as preheated liquid in the base of the column. The first alcohol feed may contain both fresh feed and recycled alcohol.

The molar ratio of the first alcohol to the carboxylic acid supplied to the column is in the range of from 1:1 to 10:1, preferably in the range of 1:1 to 5:1, more in particular in the range of 1:1 to 2:1.

The molar ratio of the second alcohol to the carboxylic acid supplied to the column is in the range of from 0.1:1 to 1:1, preferably from 0.1:1 to 0.3:1.

Where both a solid acid catalyst and a solid base catalyst are present in the reaction zone, the ratio between the two types of solid catalysts will depend on the feedstock composition, the activity of catalysts, as well as on the target conversion of the transesterification reaction. In general, in this embodiment the catalyst zone will contain 10-90% of solid acid catalyst and 90-10 wt.% of base catalyst. Preferably, the catalyst zone will contain 30-50% of solid acid catalyst and 70-50 wt.% of base catalyst, which should ensure more than 99 % conversion of the FFA and a substantial conversion of triglycerides. Base solid catalyst zone can be extended up to reboiler, inclusive, in order to take advantage from higher temperature.

In some embodiments of the fatty acid ester conversion process of the present invention it may be desired to increase the conversion of triglycerides to esters. This may, for example be the case where the conversion is not complete for kinetic and chemical equilibrium reasons. In this case it may be desired to subject the product of the reactive distillation process to a further transesterification process in an appropriate reactor system with intermediate glycerol re-

moval. Accordingly, in one embodiment the present invention
pertains to a process wherein the outlet from the reactive
distillation column is submitted to transesterification of
glycerides to fatty acid esters in the presence of a solid
base catalyst, at a pressure of about 5 to 10 bar above the
bubble point pressure of the reaction mixture at the reaction
temperature. In a preferred embodiment, this process is car-
ried out in at least two steps, with intermediate removal of
glycerol.

The use of tubular reactors for carrying out the
transesterification of glycerides in liquid phase with C1-C4
alcohols at has been already described as in EP198243-B1. Ra-
tios 10:1 up to 100:1 are claimed but no details are given
about practical implementation. On the other hand the tubular
reactor as adiabatic fixed bed column is applied in AXENS/FPI
technology, as show in the European patent EP1505048. How-
ever, employing fixed bed column reactors is constraint by
the limited residence time and hydraulic parameters that can-
not cope with the large variability of operating conditions
needed when handling waste lipid material.

In one embodiment of the present invention, for
overcoming the above limitations this invention makes use of
multi-segmented tubular reactor with a large ratio
length/diameter above 100:1 capable to ensure longer resi-
dence time. The tubular reactor is placed in a high
temperature chamber, which may, for example, be a furnace
heated up by the combustion of gas or liquid fuel.

In a preferred embodiment the reactor consists of a
number of equal tubular segments assembled such to shape a
reaction coil. The tubular reactor described before has a ra-
tio length/diameter of 100:1 to 1500:1, more preferably of
100:1 to 600:1. The tubes can be placed horizontally or ver-
tically. The initial part of the tube can serve for

preheating the reaction mixture up to the reaction temperature. In this way the reactor length can be adapted easily for changing the operating conditions, namely temperature and residence time, imposed by the large variability of the waste lipid materials, as well as to the kinetic property of a particular solid catalyst.

Since getting high conversion, over 95%, and low content of di- and mono-glycerides is limited by the chemical equilibrium, the transesterification reaction is carried out in several stages, usually two, with intermediate glycerol removal. On the other hand, the segregation of a glycerol phase depends heavily on the compositional pattern of the mixture, which in turn is determined by the initial lipid feedstock. Pushing the conversion in the first stage to high values is necessary, over 80% but preferable up to 90%.

An example of this embodiment of the present invention is illustrated in Figure 2. The bottom product from the reactive distillation section (stream 1) is mixed with first alcohol (stream 2) such to ensure convenient molar ratio alcohol/triglycerides between 3 and 30, more preferably between 9 and 12. The resulting mixture is submitted to pressure raise by the pump (P-1), which should be preferably 5 to 10 bar higher than the corresponding bubble pressure value. Then the resulting mixture enters the tubular reactor (R-1) hosted in the furnace F, where the mixture is brought to reaction temperature. The tubular reactor contains a solid base catalyst. Solid base catalysts are known in the art, and include those mentioned above. The reaction temperature depends on the nature of the catalyst. For an example, the solid base catalyst is a hydrotalcite. In this case the reaction temperature may be, for example, in the range of 150 to 250 °C, more preferably 180 to 210°C. The determination of the appropriate reaction temperature is within the scope of the skilled person.

The outlet mixture from (R-1) is sent to the heat
exchanger (H-1) for temperature reduction in counter-current
with the cold feed for the second reactor. In his way (H-1)
contributes to energy saving. After pressure reduction in (V-
5   1) down to a few bars the mixture is submitted in the unit
(S-1)to the partial removal of the light alcohol (stream 4)
to facilitate the formation of a glycerol phase. The separa-
tion technique can be a simple flash or a sequence of
flashes. The liquid phase (stream 5) is cooled in (H-2) to a
10 suitable temperature, typically around 40 C, where phase
separation occurs. The separation of glycerol phase (stream
6) takes place in the unit (S-2), by decantation or centrifu-
gation. The stream 7 is submitted to the second stage
transesterification in the tubular reactor (R-2), after alco-
15 hol make-up (8), pressure raise by the pump (P-2) and
preheating in (H-1) with the outlet from (R-1). The trans-
esterification in (R-2) should proceed to more than 95%
conversion, preferably to more than 97% conversion in such
way that the cumulative content of mono- and di-glycerides
20 becomes lower than 2 wt.%. The effluent from the reactor (R-
2) is submitted to pressure reduction in (V-2), deep light
alcohol recovery in (S-3), heat exchange in (H-3), glycerol
separation in the unit (S-4), glycerol removal through line
(12), and purification in the unit (S-5), which is usually a
25 vacuum distillation column. The biodiesel is got as the fatty
ester stream (14), while in the top (13) and bottom (15)
streams light and heavies impurities are removed.

In this way the combination of the embodiments de-
scribed in the figures 1 and 2 allows handling any free fatty
30 acids and glycerides feedstock to biodiesel.

It is noted that the base catalyst driven trans-
esterification process carried out using two (or more)
tubular reactors in an over is applicable not only to feed-
stock generated by the reactive distillation process of the
35 present invention, but also to other feedstock containing

tri-glycerylesters of fatty acids in combination with fatty acid esters of mono-alcohols.

CLAIMS

1. A process for the manufacture of acid esters
through reactive distillation, wherein a carboxylic acid is
submitted to esterification in a reaction section of a reac-
tive distillation column with an alcohol in the presence of a
5 solid acid catalyst to form an acid ester, wherein a first
supply stream comprising the carboxylic acid, a second supply
stream comprising a first alcohol and a third supply stream
comprising a second alcohol, the second alcohol having a
higher molecular weight than the first alcohol, are supplied
10 to the reactive distillation column, wherein the first supply
stream is supplied to the column at a first entry level lo-
cated just above or at the top of the reaction section, the
second supply stream is supplied to the column at a second
entry level located in or just below the reaction section and
15 below the first entry level, and the third supply stream is
supplied to the column at a third entry level located above
the first entry level, and wherein a bottom stream comprising
the ester formed is obtained and a top stream comprising un-
reacted first alcohol, water and unreacted second alcohol is
20 obtained.

2. A process according to claim 1 wherein the
carboxylic acid is a fatty acid, in particular a fatty acid
selected from C10-C18 fatty acids and mixtures thereof, and
25 the first supply feed is a fatty acid rich feedstock, in par-
ticular a feedstock which comprises C10-C18 fatty acids and
triglycerides of C10-C18 fatty acids.

3. A process according to claim 1 or 2, wherein
30 the first alcohol is selected from methanol, ethanol, propa-

nols, and mixtures thereof, more particularly methanol and ethanol.

4. A process according to any one of the preceding claims, wherein the second alcohol is selected from mono-alkyl-alcohols with 4 to 10 carbon atoms, in particular 6 to 8 carbon atoms, more particularly 2-ethyl-hexanol.

5. A process according to claim 2, wherein the fatty acids are present from 1 to 100 wt.% in a first supply stream which comprises lipid material derived from waste fats, as frying and cooking fats and oils, edible and non-edible vegetable oils, animal fats, tall oil, algae oil, or mixtures thereof, including recycled fats and oils.

6. A process according to any one of the preceding claims, wherein the molar ratio of the first alcohol to the carboxylic acid supplied to the column is in the range of from 1:1 to 10:1, preferably in the range of 1:1 to 5:1, in particular in the range of 1:1 to 2:1 and wherein the molar ratio of the second alcohol to the carboxylic acid supplied to the column is in the range of from 0.1:1 to 1:1, preferably from 0.1:1 to 0.3:1.

7. A process according to any one of the preceding claims, wherein the reaction section comprises a solid acid catalyst, optionally in combination with a solid base catalyst, located below the solid acid catalyst.

8. A process according to any one of the preceding claims wherein the pressure in the reactive distillation column is between ambient pressure and 20 bar, in particular between 2 and 6 bar and the temperature in the reaction sec-

tion is between 100 and 220°C, in particular between 130 and 180°C.

9.   A process according to any one of the preceding claims, wherein the product stream containing the ester formed is subjected to a distillation step to remove unreacted first alcohol, which may be recycled to the distillation unit.

10.   A process according to any one of the preceding claims, wherein the top stream product is subjected to a liquid-liquid phase separation by decantation wherein the organic phase containing the first and the second alcohol is separated and recycled to the distillation unit and the water phase separated and sent to waste water treatment or / and first alcohol recovery.

11.   A process according to the claim 10 wherein the third supply stream enters the decanter of the reactive distillation column on level control.

12.   A process according any one of the preceding claims wherein the outlet from the reactive distillation column is submitted to transesterification of glycerides to fatty acid esters in the presence of a solid base catalyst, at a pressure of about 5 to 10 bar above the bubble point pressure of the reaction mixture at the reaction temperature.

13.   A process according to claim 12, wherein the transesterification of glycerides to fatty acid esters takes place in a multi-segment tubular reactor where the length to diameter ratios is 100:1 to 1500:1, more preferably 100:1 to 600:1.

14. A process according to claim 12 or 13 wherein the reaction is carried out in at least two steps with intermediate removal of glycerol.

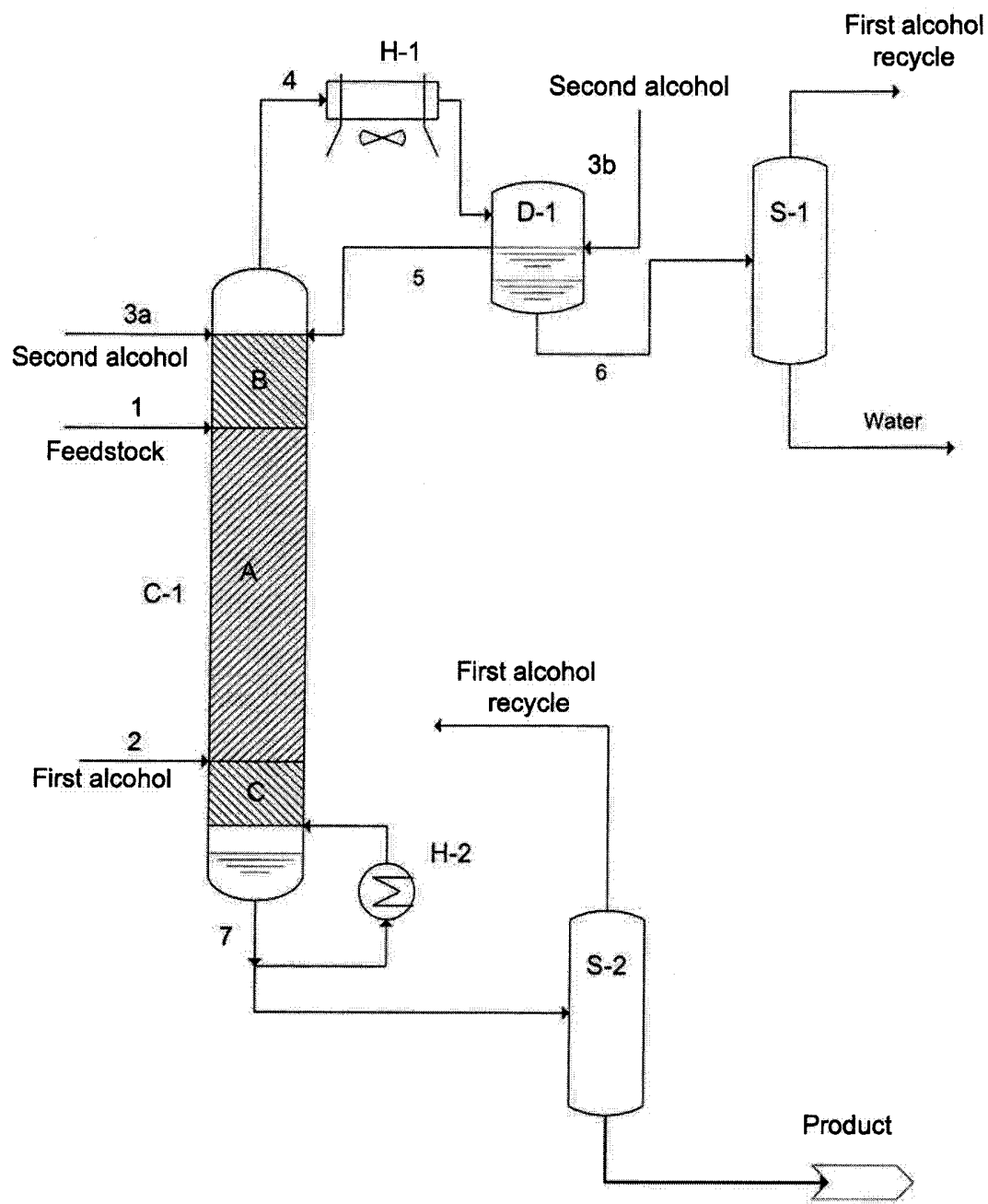15. A process according to any one of claims 13 or 14 wherein the tubular reactor is placed in a fired furnace
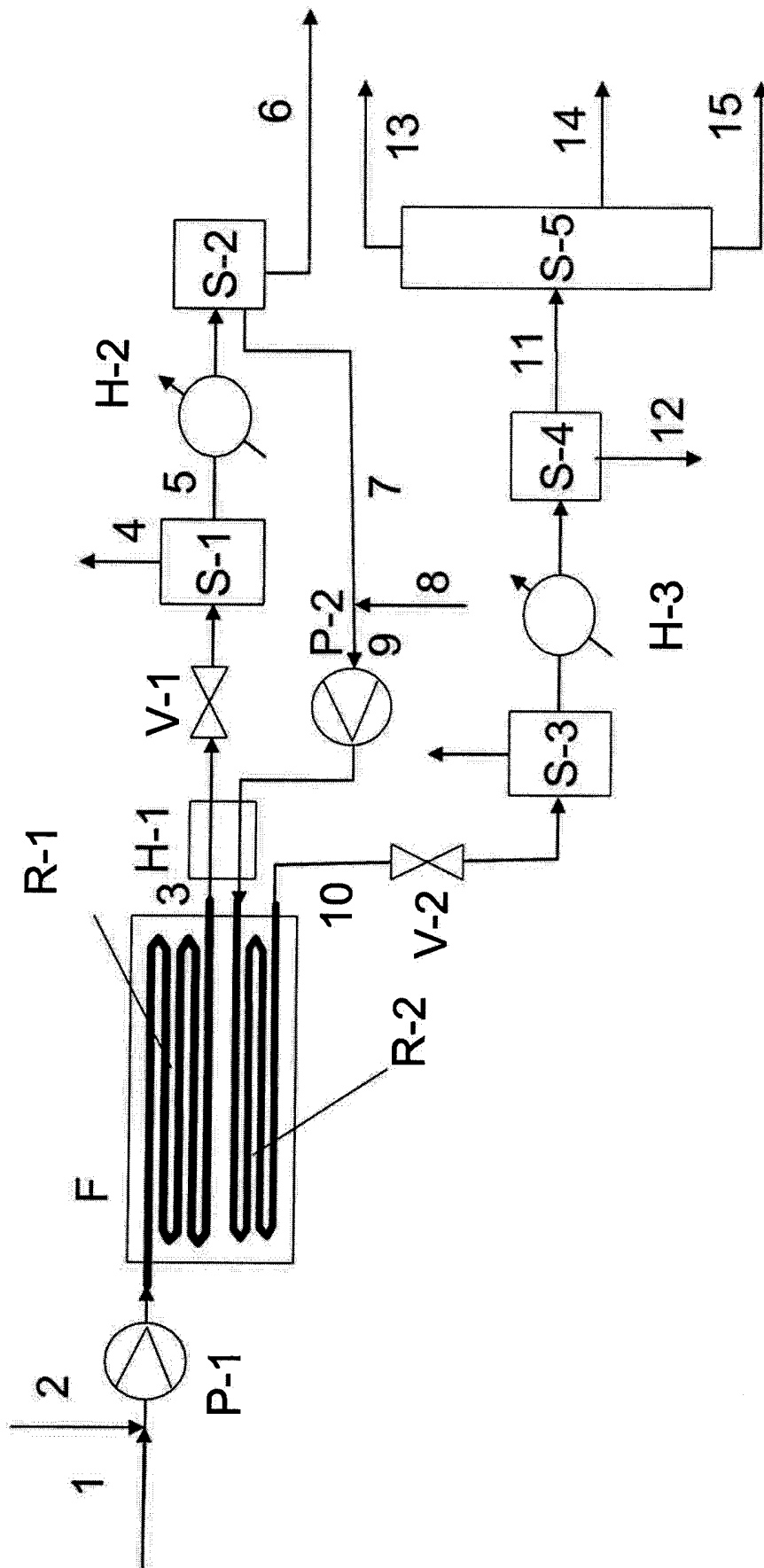
Figure 1

Figure 2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10L1/19   C10L10/12   C10L1/02   C07C67/03   C11C3/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10L   C07C   C11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KNOTHE G ET AL: "Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester<*>" FUEL, IPC SCIENCE AND TECHNOLOGY PRESS, GUILDFORD, GB, vol. 82, no. 8, 1 May 2003 (2003-05-01), pages 971-975, XP004413533 ISSN: 0016-2361 cited in the application	1-13
A	EP 0 198 243 A (HUELS CHEMISCHE WERKE AG [DE]) 22 October 1986 (1986-10-22) cited in the application claim 3	13

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| X | Further documents are listed in the continuation of Box C. | | X | See patent family annex. |

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 October 2009	30/10/2009

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C(Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	A.A. KISS ET AL: "The Heterogeneous Advantage: Biodiesel by Catalytic Reactive Distillation" TOPICS IN CATALYSIS, vol. 40, no. 1-4, 1 November 2006 (2006-11-01), pages 141-150, XP002511729 paragraph [0002]	1-15

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