



# Hydrodeoxygenation, decarboxylation and decarbonylation reactions while co-processing vegetable oils over a NiMo hydrotreatment catalyst. Part I: Thermal effects – Theoretical considerations



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## HIGHLIGHTS

- Processing of fatty oils and natural fats into paraffinic biodiesel components.
- The triglycerides conversion routes – the secondary exothermic methanation reaction.
- The conversion parameters change contribution of main and secondary reactions.
- The influence of the different conversion routes on the total thermal effect.

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## ABSTRACT

The presented work covers theoretical considerations regarding the total heat effects associated with vegetable oil hydroconversion to form n-paraffinic diesel fuel biocomponents relative to the process conditions. The hydroconversion of fatty acid triglycerides is a highly exothermic process. The hydrodeoxygenation, decarboxylation and decarbonylation of fatty acids are the basic reactions occurring during this process. The hydrodeoxygenation and decarboxylation reactions are exothermic, while decarbonylation exhibits a relatively modest endothermic effect. A similar situation applies to the secondary reactions: rWGS – reverse water gas shift reaction (endothermic) and CO methanation (strongly exothermic). The contribution of each reaction depends on the process conditions, particularly the hydrogen pressure. Theoretical considerations suggest that the total heat effect in the reactor should be similar under different pressure conditions. The heat effects connected to a particular hydroconversion reaction (main and secondary) may compensate one another.

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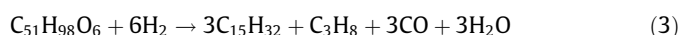
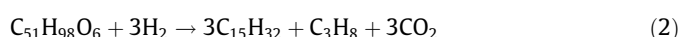
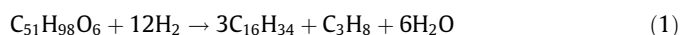
## 1. Introduction

Processing vegetable oils and fats into fuel cuts is currently the subject of intense research worldwide [1–24]. Consequently, commercial processes for hydroconverting triglycerides into n-paraffins have been developed. The NExBTL process developed by Nested Oil is one such technology. During this process, pure (100%) vegetable oils and fats are converted [3,4]. The production of second generation biofuels via co-processing fats and vegetable oils with petroleum cuts during conventional refining processes is described in [5–13]. This process can be realised as a hydrotreatment (hydroconversion) or FCC process [8,24].

Co-processing vegetable oil – crude oil middle distillate mixtures does not differ significantly from the hydroconversion of pure

triglycerides; however, during this process, the hydrorefining of the hydrocarbon feedstock (hydrodesulphurisation (HDS), hydrodenitrogenation (HDN) and aromatic hydrogenation (HYD)) occur alongside the hydrodeoxygenation, decarboxylation and decarbonylation processes [14]. Oxygen elimination (HDO) reactions are accompanied by the hydrogenation of the double bonds in the fatty acid chains on the triglycerides. Therefore, co-processing is a chemically complicated process but remains a very interesting research subject.

The equations for the HDO reactions exemplified by palmitic triglyceride are presented below:



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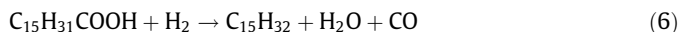
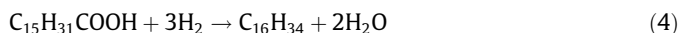
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The mechanism of hydrotreatment reactions of vegetable oils is complex and consists of a series of consecutive steps. Melis [14] claims that triglyceride conversion begins with the hydrogenation of the double bonds in the hydrocarbon chains of the fatty acids before the decomposition of the triglyceride structures to form fatty acids and propylene occurs.

The conversion of fats and vegetable oils occurs over typical NiMo or CoMo hydrotreatment catalysts. The produced paraffins can be used as a base bio-component for diesel oil. Because the low temperature properties of these paraffinic fractions are poor (relatively high cloud and pour points), they are usually subjected to isomerisation [3].

## 2. Reactions for triglycerides conversion

Triglyceride hydroconversion is a multistage process [14–16]. During the first stage, the double bonds in the fatty acid chains on the triglycerides are hydrogenated. Next, the hydrogenated glycerides crack to form fatty acids and propylene; under high pressure with excess hydrogen, propylene is hydrogenated to form propane. Afterward, the fatty acids are hydroconverted according to the reactions below for palmitic acid: hydrodeoxygenation (4), decarboxylation (5) and possible decarbonylation (6).



Equilibrium between the CO and CO<sub>2</sub> is reached, according to reaction (7):



Because of this equilibrium, the decarbonylation and decarboxylation (6) reactions are not independent [14]. According to [14,15], methanation (CO removal through a reaction with H<sub>2</sub>) is strongly exothermic, possibly increasing the temperature in the reactor significantly (Δ*T*) to cause local overheating in the catalyst bed. This reaction also increases hydrogen consumption; the additional amount of hydrogen may vary between 20 and 35 N m<sup>3</sup>/m<sup>3</sup> (for a feedstock containing 10% vegetable oil).

### 2.1. Heat effects of triglycerides hydroconversion and secondary reactions

The hydrodeoxygenation and decarboxylation reactions on triglycerides with concurrent hydrogenation of the double bonds in the fatty acids chains are exothermic [14]. The enthalpy of the individual reactions may be calculated using the following equation (8).

$$\Delta H_{\text{reaction}} = \sum n_i \Delta H_{\text{products}} - \sum n_j \Delta H_{\text{reactants}} \tag{8}$$

The enthalpy for fatty acids and triglycerides formation are not commonly available. In our work for calculation, combustion heat values were adopted [17]. For the other reagents, the Δ*H* values were taken from a ChemCad database. The enthalpy values are presented in Table 1.

The hydroconversion process of oleic triglyceride according to the mechanism proposed by Melis [14] will be as follows (9):



In accordance with publications [14,15] enthalpy for triglycerides hydrogenation amounts −303 kJ/mol.

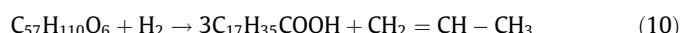
Next fatty acids and propylene are formed by cracking a completely hydrogenated triglyceride (10). A reaction using stearic

**Table 1**  
Standard heats of formation for fatty acids (C<sub>18</sub>) present in fatty oil triglycerides, water and n-paraffins obtained after hydroconversion.

Compound	Molar heat of conversion Δ <i>H</i> <sup>0</sup> (kJ/mol)
Stearic acid	−763
Oleic acid	−671.3
Linoleic acid	−540
Linolenic acid	−405
H <sub>2</sub> O (gas)	−239.3
CO	−110.5
CO <sub>2</sub>	−393.5
CH <sub>4</sub>	−74.9
Propane	−104.7
<i>n</i> -Heptadecane	−393
<i>n</i> -Octadecane	−414
Propylene CH <sub>2</sub> =CH−CH <sub>3</sub>	+20.4
Stearic triglyceride C <sub>57</sub> H <sub>110</sub> O <sub>6</sub>	−2520 <sup>a</sup>
Oleic triglyceride C <sub>57</sub> H <sub>104</sub> O <sub>6</sub>	−2217 <sup>a</sup>

<sup>a</sup> [17].

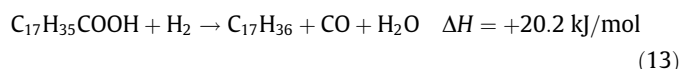
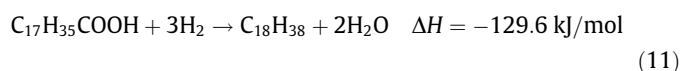
triglyceride (completely hydrogenated chains of fatty acids) as an example will occur as follows:



The total heat effect of propylene hydrogenation (10) will equal value of +251 kJ/mol.

During the next stage, the hydrogenated fatty acids formed due to the decomposition of the triglycerides are deoxygenated through three possible reactions (4)–(6), forming n-paraffins with different chain lengths.

The enthalpy of the stearic acid hydrodeoxygenation (11), decarboxylation (12) and decarbonylation (13) will be as follows:



The highest exothermic heat effect (from the three considered reactions of fatty acids deoxygenation) is associated with hydrodeoxygenation. The exothermic effect of the decarboxylation reaction is much lower than the heat effect of the hydrodeoxygenation reaction. On the contrary, fatty acid decarbonylation may be endothermic (provided it occurs).

Donnis et al. [16] claim that, “the water gas shift activity of the catalyst makes it difficult to establish whether the observed CO and CO<sub>2</sub> are produced by decarboxylation... or by a similar decarbonylation route as proposed in the literature”, e.g. [24].

The decarbonylation reaction (13) can be recognised as the joining of decarboxylation (12) and rWGSR (15) reactions [17]. Similarly, the CO<sub>2</sub> methanation reaction specified by Veriansyah [18] can be recognised as the joining of two reactions: rWGSR (15) and CO methanation (16).

### 2.2. Enthalpy (Δ*H*) of the hydrogenation reaction

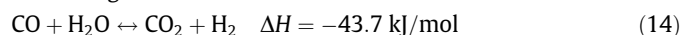
Based on the calculated enthalpies (Δ*H*) of the reactions, the hydrogenation of double bonds in the fatty acids chains on triglycerides (9), the decomposition of these triglycerides to saturated fatty acids and propylene (10), and the hydrogenation of propylene to propane (17) are classified as secondary reactions; reactions (9) and (17) are accompanied by relatively high heat effects. In contrast, reaction (10) is endothermic.

When using oleic triglyceride as a model, the formation of one stearic acid molecule is accompanied by a heat release of approximately 220 kJ/mol. Oleic acid contains one double bond in the hydrocarbon chain; linoleic acid has two, and linolenic acid has three. Therefore, the hydrogenation of linoleic or linolenic triglycerides will be associated with much higher exothermic effects than during oleic triglyceride hydrogenation. These reactions consume a significant amount of hydrogen.

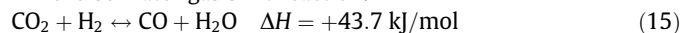
### 2.3. Enthalpy ( $\Delta H$ ) of the secondary reactions

In accordance with [14,15], the following secondary reactions that occur during triglyceride hydroconversion and their enthalpies may be given as follows:

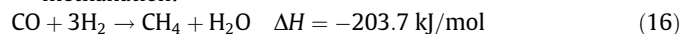
– water gas shift reaction:



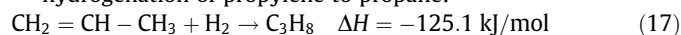
– reverse water gas shift reaction:



– methanation:



– hydrogenation of propylene to propane:



The water gas shift reaction (WGSR) and the reverse water gas shift reaction (rWGSR) are equilibrium reactions. According to some authors, the value of  $\Delta H$  for the water gas shift reaction is  $-41.2 \text{ kJ/mol}$  [25].

NiMo catalysts exhibit significant selectivity when converting carbon monoxide into methane [14,15]. The large excess of hydrogen relative to the other reagents and relatively high pressure also favour methanation. The equilibrium for the water gas shift reaction will be shifted toward the formation of additional carbon monoxide, making the probability of this reaction occurring is very low. The reverse water gas shift reaction will also occur meaning that the water formed in the system will not be converted

[14,15]. This is important in the context of the total heat effect that may occur in the reactor during triglyceride hydroconversion because the reverse water gas shift reaction is endothermic.

### 2.4. The resultant heat effect in the reactor according to process parameters

The three basic reactions of hydroconversion for fatty acids (formed as a result of hydrogenation of double bonds in chains of these acids and decomposition of triglycerides structures) may be identified. The first reaction is the hydrodeoxygenation of a hydrogenated fatty acid molecule without removing a carbon atom (11). The total heat effect for stearic acid hydroconversion was calculated as an example. The hydrodeoxygenation of stearic acid (11) is associated with the largest exothermic effect ( $-129.6 \text{ kJ/mol}$ ). The products of this reaction do not undergo secondary reactions.

The second reaction is the decarboxylation of a fatty acid molecule with one carbon atom removed as  $\text{CO}_2$  (12). The carbon dioxide may participate in secondary reactions (reverse water gas shift reaction) (15) to form CO.

The third possible reaction is associated with the decarbonylation of a fatty acid molecule (13) to form CO and  $\text{H}_2\text{O}$ .

Carbon monoxide produced via decarbonylation or decarboxylation + rWGSR may undergo further hydrogenation to form methane reaction sequences (18) and (19).

decarboxylation  $\rightarrow$  reverse water gas shift reaction



For stearic acid, the total effect of this reaction sequences (18) and (19) will approach  $-180 \text{ kJ/mol}$ . Therefore, regarding the heat effect, whichever reaction sequence occurs (with decarboxylation or with the possible decarbonylation) does not matter. This exothermic effect for reaction sequences (18) and (19) is approximately 1.4 times larger than for hydrodeoxygenation. The hydrogenation of propylene to propane (17) should also be accounted for. Although

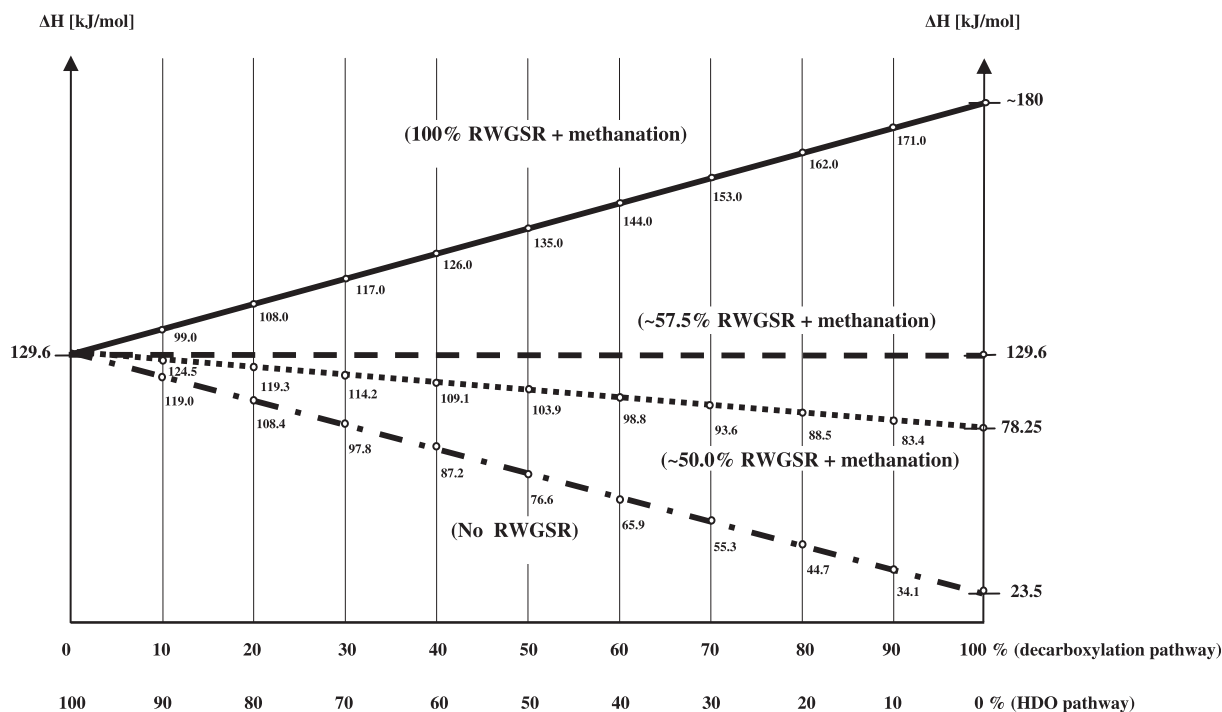


Fig. 1. Theoretical heat effect connected to the hydroconversion of stearic acid versus the contribution of decarboxylation, hydrodeoxygenation (HDO) and secondary reactions (rWGSR and methanation).

the reaction is not as strongly exothermic as methanation, it occurs on a much larger scale, possibly exerting a large influence on the total heat effect. The consumption of hydrogen in the above reactions is worth considering. Each of the hydrodeoxygenation reactions of the hydrogenated molecule of an acid needs three moles of hydrogen, while the entire reaction sequence in (18) and (19) consume four moles of hydrogen. To what extent are the individual mechanisms of the hydroconversion and associated chemical reactions responsible for the final heat effect generated in the reactor? Most likely, this heat effect depends on the contributions of the individual reactions for the hydroconversion reactions (11)–(13); these reactions depend on the process conditions and the characteristics of the catalyst used during the process. Therefore, it may be hypothesised, that a higher contribution of decarboxylation and decarbonylation reactions (forming directly CO), potentially generates a larger total heat effect.

However, the problem is more complicated because the extent of the strongly exothermic secondary reactions (e.g., methanation) must be considered. Egeberg [15] claims that during the hydroconversion of a feedstock consisting of a Middle East SR LGO (75 vol.%) and rapeseed oil (25 vol.%) over a NiMo catalyst (at 350 °C, under 45 bar, with a 1.5 h<sup>-1</sup> LHSV and a ratio of hydrogen : feedstock equal to 500 N m<sup>3</sup>/m<sup>3</sup>), approximately 50% of the carbon dioxide was converted into CO, and 30% of this amount underwent methanation. Therefore, it should be marked, that this result was obtained for specific type of feedstock and over the selected catalyst.

The theoretical thermal effect of the hydroconversion depends on the individual contributions of the enthalpy of the reactions taking place in the process. In this study, the calculations were made for stearic acid. Fig. 1 depicts the magnitude of the total theoretical heat effect generated in the reactor during the hydroconversion of stearic acid. The dotted – dashed lines labelled ‘No rWGSr’ show the magnitude of the total heat effect when assuming that during the hydroconversion of this compound, only hydrodeoxygenation and decarboxylation reactions occur. The line labelled ‘100% RWGSr + methanation’ shows the magnitude of the total heat effect when assuming that the total amount of carbon dioxide formed via decarboxylation is converted into carbon monoxide by the RWGSr and that the carbon monoxide is completely converted into methane. The dotted line labelled ‘50% RWGSr + methanation’ shows the magnitude of the total heat effect when assuming that 50% of the carbon dioxide formed via decarboxylation is converted to carbon monoxide due to the RWGSr and that all of the carbon monoxide undergoes total methanation. Some researchers [15] show that this situation is the most probable. The line shows that, despite the variable contributions of hydrodeoxygenation and decarboxylation, the total heat effect in the reactor does not change significantly. The line will remain horizontal (a value of total  $\Delta H$  will not change) when the conversion of carbon dioxide to carbon monoxide will be approximately 57.5% (dashed line in Fig. 1 labelled ‘~57.5% rWGSr + methanation’).

### 3. Conclusions

The heat effect connected to CO methanation is relatively large compared to the heat effects of the other reactions that occur during triglyceride hydroconversion; therefore, this reaction is likely the primary cause of the temperature increases in the hydroconversion reactor [14,15]. However, methanation depends on decarboxylation and/or decarbonylation reactions, and their enthalpies are many times lower than the hydrodeoxygenation reaction enthalpy. These facts indicate that the heat effect changes caused by altering the contribution of the individual reactions in the process may compensate for one another. For example, increasing the process pressure inhibits decarboxylation and/or decarbonylation

reactions, diminishing the amount of carbon monoxide formed by decarbonylation and the rWGSr before methanation. These conditions may decrease the heat effect compared to the heat effect that occurs at lower pressures. The final value will be strongly affected by the degree of carbon dioxide conversion into carbon oxide and the influence of the increased pressure on the methanation equilibrium; methanation is favoured by high pressure. Nevertheless, the increased pressure simultaneously favours the strongly exothermic hydrodeoxygenation; the lower heat effect attributed to the lower degree of methanation may be offset by the increased hydrodeoxygenation heat effect.

If less than ~57.5% of the hydroconversion reactions are triglycerides decarboxylation reactions while assuming that the total amount of CO<sub>2</sub> formed in this reactions is subjected to rWGSr followed by methanation, the total heat effect in the reactor is equal to or lower than heat effect of the hydrodeoxygenation reaction alone (see Fig. 1).

Therefore, the total heat effect in the reactor associated with the hydroconversion performed under different pressures should be similar for the same vegetable oil. However, the heat effects connected to the hydroconversion of two vegetable oils with varied unsaturated fatty acid contents in the triglycerides should differ noticeably.

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