

Thermodynamic Study of Batch Reactor Biodiesel Synthesis

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Based on thermodynamic considerations, it is demonstrated that the excess of methanol is not required for reaction shifting towards biodiesel synthesis, but to promote the mixing of reactants. The excess of methanol added to promote the mixing of reactants must be eliminated to a low amount as otherwise the phase split of products is not favourable. It is more favourable to expend energy on mixing than recovering a high excess of methanol. The study covers the main units used in batch production of biodiesel: mixing, reaction, distillation and decanter.

Keywords: methanol excess, biodiesel synthesis, thermodynamics

A process design is feasible only if the mass and energy balances and thermodynamic principles are fulfilled (e.g. conservation of mass and energy). Some additional conditions are specific for some units such as, for distillation, a composition column profile between the distillate and bottoms must exist, e.g. infinite/infinite analysis [1]. Usually, multiple feasible alternatives can be proposed and a detailed study of all them would be very time consuming and therefore simplified models are often used. The second step is therefore to check the potential of each one and discard the least promising ones. For instance, to determine the minimum hot and cold utilities required for a process, it is not necessary to define a detailed heat exchanger network, but just to take into account the second thermodynamic principle, e.g. pinch analysis [2].

A deep understanding of a process can only be achieved when conservation and thermodynamic principles are checked and well understood. Therefore some basic concepts on thermodynamics are here provided. Any process stream can be completely defined using four thermodynamic variables, e.g. the equation of state of a gas can be defined by pressure, volume, temperature and number of moles. These variables are commonly used because they are easily measurable, but there are some other not directly measurable, but calculable and useful for calculations, e.g. entropy and chemical potential. The above mentioned variables can be divided into intrinsic and extrinsic, depending on its dependency or not on the quantity of matter, e.g. the volume is extrinsic and the pressure is intrinsic. The thermodynamic variables not measurable and not used outside the scientific world are usually more difficult to understand. In a simple way, they can be situated in a simple scheme as follows: by analogy, as volume and pressure are the extrinsic and intrinsic measurement of the same energy aspect, then the entropy is the extrinsic variable corresponding to the intrinsic variable temperature and the chemical potential is the intrinsic variable corresponding to the extrinsic variable number of moles. Figure 1 shows graphically the above mentioned variables.

As mentioned above, there are only four independent variables. The variables are interrelated in the following way: the variation of a first variable versus a second variable in the same octahedral edge (keeping constant the other

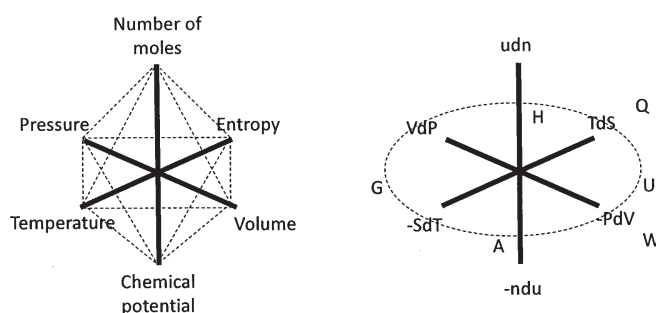


Fig. 1. Thermodynamic intrinsic (up-left) and extrinsic (down-right) corresponding variables and their product energies

edge connected variables to the second variable) is equal to the variation ratio of the variables present in the opposite edge, e.g.

$$\left. \frac{dP}{dT} \right|_{v,n,u} = \left. \frac{dS}{dV} \right|_{T,n,u} \quad (1)$$

When the corresponding intrinsic and extrinsic variables are multiplied, energy is obtained as result, e.g. heat ($Q=T \cdot dS$) or work ($W=P \cdot dV$). Therefore, the product of the corresponding intrinsic and extrinsic variables resumes the ways in which the energy can be presented in a stream. The absolute values are not relevant, only the increase of energy between input and output streams is significant. To simplify the energy calculations, three thermodynamic variables are kept constant, remaining one degree of freedom. Depending on the variables kept constant, the resulting energy is called Helmholtz (A), internal (U), enthalpy (H) or Gibbs (G) (fig. 1). From the process point of view, the chemical engineers usually use the enthalpy (eq. 2) and Gibbs (3) energies because most of the industrial chemical processes take place at constant pressure, and its corresponding term becomes simplified. Enthalpy is used for heat energy balances and Gibbs energy is used to check if the process is spontaneous or not. The Gibbs energy corresponds to the energy variation when all the intrinsic variables are in the differential part of the equation. Most commercial simulators provide the entropy and enthalpy in the stream results. Although the values can be different, for different simulators, according to the reference condition taken into account for its calculation, the increment between input and output streams are the same.

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$$dH = V \cdot dP + T \cdot dS - nd \cdot U \quad (2)$$

$$dG = V \cdot dP - S \cdot dT - nd \cdot U \quad (3)$$

When the process is isobaric and isothermal then dP and dT are zero, and from equations 2 and 3 there is obtained equation 4, whose values are provided by commercial simulators. The Gibbs energy, when there is not vapour phase, can be also calculated using Equation 5, which is used in many papers. Lets consider n_p – number of phases, n_c – number of compounds, γ – activity coefficient and x – mole fraction. The activity coefficient is calculated using thermodynamic models such as NRTL or UNIQUAC or using group estimation methods such as UNIFAC.

$$dG = dH - TdS \quad (4)$$

$$\frac{G_{III}}{RT} = \sum_{k=1}^{n_p} \sum_{i=1}^{n_c} n_i^{L(k)} \left[\ln(x_i^{L(k)} \gamma_i^{L(k)}) \right] \quad (5)$$

The equation 4 is used in the present paper to check the spontaneity of the process. However, a non spontaneous process does not imply that is not feasible, but that additional energy is required to accomplish it. For instance, a distillation column decreases the entropy of the streams by consuming energy with an efficiency according to the Carnot efficiency, i.e. a distillation column is a thermal machine that instead of work produces a decrease of entropy [1]. Equation 5 is also useful to calculate the equilibrium conditions when the Gibbs energy is zero, (e.g. to determine the equilibrium compositions of two liquid phases in equilibrium), or minimized, (e.g. to estimate the chemical equilibrium composition for a reaction system) [3]. Presently, the liquid-liquid equilibrium in decanter is solved by checking the equality of activity of each component in the two liquid phases. The solution obtained by this method may not correspond to the stable steady state [4]. The stable steady state solution corresponds to a minimum value of Gibbs free energy function, which can be without phase split, meanwhile the simulator is able to converge a solution satisfying the equation 5 and therefore assuming that there is a phase split.

To illustrate the use of Gibbs energy and thermodynamics to determine the usefulness of process integration, the biodiesel synthesis is studied. In European Union, Directive 2009/28/EC requires since 2008 by law that every year the production of biofuels increases, with the aim that by 2020 10% of transport fuels to be biofuels, USA future plan for biodiesel production is around 3.3 million tons in 2016 [5], India plans a 10% mix in the total diesel consumption (60.14 million tons during 2009 - 2010) and this increasing biodiesel demand politics is also applied in many other countries all-over the world. As a consequence of this concern, an intense research is performed in this field to provide biodiesel in the best process conditions, which is reflected by the thousands of papers available.

There are different kinds of vegetal oil modification methods, such as dilution, thermal cracking (pyrolysis), trans-esterification, and microemulsification, to make them useful in nowadays diesel engines. However, transesterification is recognized as the most appropriate method for producing higher quality biodiesel [6] and therefore we will focus also on it. The transesterification of oil with an alcohol presents as main drawback that the reactants (oil/alcohol) are immiscible. In most of the papers in literature, methanol is used as reactant and the

main focus is on the reaction, trying to reach a high enough conversion to satisfy the biodiesel purity requirements. In some papers, no kinetic data is provided, and just the maximum conversion obtained by certain catalyst in certain operation conditions are given. The conversion depends on the catalyst or enzyme, and kind of oil used, but usually an excess of methanol is used. The excess of methanol is around 2 and 3 times its stoichiometric value. The reactor temperature is usually between 50 and 65°C, but the main heating energy costs are derived from the methanol recovery. Usually with a 0.5 to 2 % wt of catalyst, the reaction reaches high enough yields in few hours. Due to the immiscibility, the reactor stirring speed influences the overall reaction time, and ultrasonic devices can also speed up the reaction time. Therefore, a great number of papers try to optimize the reactor without an overall view of the problem. The goal of the present paper is to provide an overall view of the biodiesel synthesis process.

Methodology

Mass balances, entropy and enthalpy of the streams are calculated using *Aspen Plus*[®] and the support example related to biodiesel synthesis available in *Aspen Plus*[®] documentation. The minimum energy required by the distillation is calculated using the equation [7]:

$$Q = \frac{T_c \cdot \Delta S_{sep}}{\eta} = \frac{T_c \cdot (T_r - T_c) \cdot \Delta S_{sep}}{T_r} \quad (6)$$

where:

$$\Delta S_{sep} = R \cdot \left[(D + B) \cdot \left(\sum x_i^{feed} \cdot \ln x_i^{feed} \right) - D \cdot \left(\sum x_i^{distil} \cdot \ln x_i^{distil} \right) - B \cdot \left(\sum x_i^{residue} \cdot \ln x_i^{residue} \right) \right] \quad (7)$$

Results and discussions

First of all, the process is divided into a classical scheme of unit operations, taken into account separately: mixing of reactants, reaction, separation of the non-reacted methanol by distillation and separation of the products by liquid-liquid equilibrium. An ideal catalyst or enzyme is assumed, where the thermodynamic equilibrium defined by the Gibbs energy is attained instantaneously with a very low amount of heterogeneous catalyst or enzyme.

Mixing of reactants

Oil is called hydrophobic (water-fearing) but although the term seems that polar compounds such as water or methanol repels oil, in fact, the separation of oil and methanol is not due to repulsion between methanol and oil molecules, but to particularly favourable hydrogen bonding between methanol molecules. Oil and methanol molecules actually attract each other, but not nearly as strongly as methanol attracts itself. In the vapour phase, the hydrogen bonds of methanol are broken, therefore the temperature favours the solubility of methanol and oil. The cost of hydrating a small, hydrophobic solute has more to do with the number of ways in which hydrogen bonds can form, than with their strength. That is, the solvation free energy of the system is largely entropic and not enthalpic [8]. On the other hand, the amount of methanol has also a great influence on the oil solubility. The free energetic cost of dissolving large oil molecule in methanol is very high, but this cost can be successfully compensated by attaching sufficient number of methanol groups to the oil. Figure 2 shows that the methanol and oil mixtures do not become miscible until temperatures higher than 55 °C, and a ratio of methanol/ oil higher than 12.

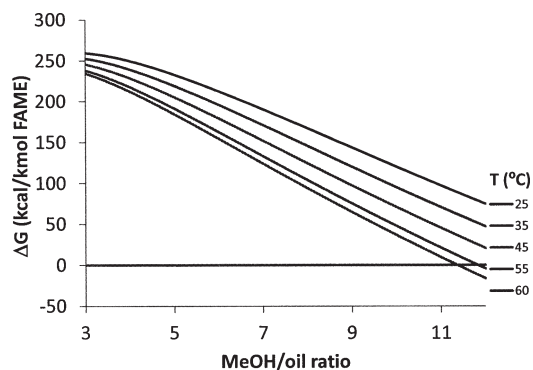


Fig. 2. Influence of reactants ratio and temperature on the solubility between reactants

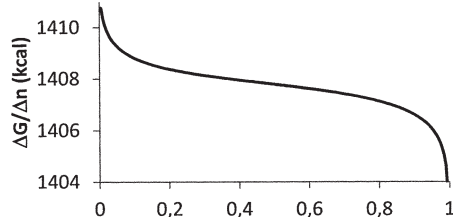


Fig. 3. Reactor conversion for a stoichiometric feed at 25 °C

However, due to the energy provided by the stirrer, the methanol hydrogen bonds can break at lower conditions. The maximum temperature is limited by the boiling point of methanol and therefore, the increases of miscibility and consequently of reaction kinetics is obtained by adding an excess of methanol. For instance, at 60 °C, the Gibbs energy at a molar methanol/oil ratio of 3 is 2.5 times the Gibbs energy at a ratio of 8. The energy of mixing is related to the stirring speed at square value, and therefore, although the energy of Gibbs is 2.5 higher, the stirring speed is just 1.58 times higher, and therefore an initial intense stirring is recommended, at least when the reactants are charged. Another way to introduce energy and break the hydrogen bonds is by ultrasounds or microwaves.

The Reaction System

Yancy-Caballero and Guirardello (2013) [9] have calculated the phase and chemical equilibrium by Gibbs energy minimization method using equation 5 for biodiesel synthesis by transesterification of soybean oil with several kinds of alcohols, also methanol. Three different estimations of the activity coefficients were used and all the chemical compounds presents in the mixture are taken into account. A high conversion was obtained also when a stoichiometric feed molar ratio 1:3 was used, even at temperatures as low as 30 °C. These results show that the excess of methanol is not required to shift the reaction towards products. However, although the reaction of oil with methanol leads to total conversion, the reaction of a fatty acid with methanol is of equilibrium, e.g. lauric acid with methanol [10]. Figure 3 corroborates a high conversion using equation 4 showing that the minimum Gibbs energy corresponds to a total conversion to products although the feed would be stoichiometric. The reaction intermediates are not taken into account, to simplify the calculation. Figure 3 is calculated at 25 °C but the same shape is obtained also at higher temperatures. The minimum indicating the equilibrium is attained at total conversion.

The decanter

Usually, the excess of methanol is recovered at the exit of the reactor, but assuming that it is feasible a total conversion at low temperature in the reactor, a decanter

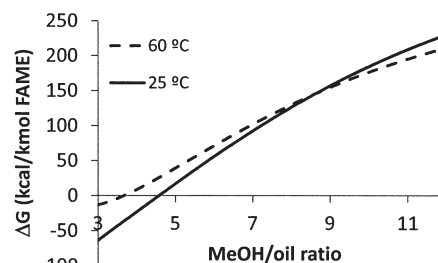


Fig. 4. Phase split stability of the reaction products

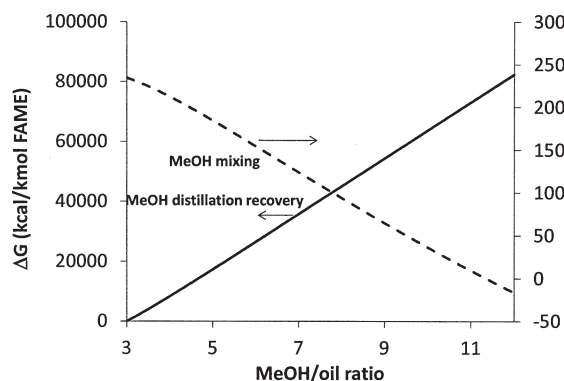


Fig. 5. Energy required to recover the methanol in excess, by distillation

after the reactor could be considered plausible. Assuming total conversion of oil, *Aspen Plus*[®] calculates a phase split for all concentrations according to equation 5. But when equation 4 is used, it is observed that a phase split in the decanter is only feasible at low ratio of reactants. The miscibility of the reaction mixture as the reaction advance from reactants to products is in agreement with the experimental observation that once the two phases were mixed with a molar MeOH/oil ratio of 6 and the reaction was started, stirring was no longer needed resulting in a stable mixture without phase split (stable emulsion) [11]. Therefore, before the decanter, the excess of methanol should be recovered by distillation. The affinity of methanol to remain in solution with FAME is greater than expected, based on the boiling points, and only when appreciable amounts of methanol are in solution, larger amounts of methanol could be removed [12].

The distillation column

The distillation column can be considered as a thermic machine that provides the required separation energy. The efficiency depends on the distillate and bottoms temperatures. The distillate temperature can be fixed at 64.7 °C according to the boiling point of methanol at atmospheric pressure. The bottoms temperature is around 300 °C due to the boiling point of a mixture of biodiesel and glycerol at molar ratio of 3:1, according to the reaction stoichiometry. The oil is not considered because is the limiting reactant. Therefore, the efficiency is around 41 %. The entropy necessary to separate the mixture divided by the efficiency and adding the energy required to evaporate and recover the methanol in the distillate provides the minimum distillation column energy requirements [8]. Figure 5 compares the energy required to separate the methanol by distillation with the energy required to mix it in the reactor. From this result can be concluded that it is better to consume energy in mixing a stoichiometric mixture than to recover the methanol by distillation. This is a clear example that reactor conditions optimization does not mean that the overall process is also optimized. An

excess of methanol favours the reaction, but its recovery consumes very high amount of energy.

Conclusions

The mixing of reactants is the main drawback in the biodiesel synthesis, and most of the energy consumed is required to recover the excess of methanol. The excess of methanol contributes mainly to help mixing the reactants, but the energy for its recovery is two orders of magnitude higher than the energy of mixing. The energy introduced by microwave or ultrasounds helps mainly to mix both phases and once the reaction starts it achieves total conversion when the ratio of methanol oil is higher than 5 to avoid a phase split at 60°C. The excess of methanol must be eliminated by distillation before the decanter to provide the desired phase split of products. The methanol is quite soluble in FAME.

Acknowledgements: The authors would like to thank the financial support of POSCCE project ID 652 (Structural Funds for Development and Cohesion).

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Manuscript received: 24.09.2013