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Material Selection of Batch Type Supercritical Reactor for Biodiesel Production

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Abstract: Non-catalytic biodiesel production using supercritical alcohol may replace time and energy-consuming catalytic biodiesel production. Production of biodiesel with supercritical methanol requires extreme process conditions such as high temperature and pressure. To enable this process to take place a batch-type reactor has been designed and constructed. Materials for the construction of high-pressure vessels should satisfy strength requirements, temperature characteristics, and corrosion resistance. Besides, these factors also availability, cost, and ease of fabrication are other factors that must be considered during material selection. Among those factors, the mechanical strength of the chosen material for pressure vessels is the most important design factor for safety operation. Small pressure vessels should be designed in such a way that the operating pressure is still too low to cause any crack to propagate in the vessel (''yield before break''). For this study, a batch type of reactor was designed with a capacity of 600 mL, and operating temperature and pressure were taken as 240˚C (513 K) and 83 bars (8.3 MPa), respectively, which were just above the critical temperature and pressure of methanol. The most common and widely used construction materials for pressure vessels are stainless steels due to their high mechanical strength, corrosion resistance, ease of availability, and low costs such as Grade 304 and Grade 316 as compared to nickel-rich alloys (such as Inconel, Incoloy, Hastelloy). As a result, 316 stainless steel was found to be the best choice of material for the reactor planned to be designed for supercritical biodiesel production.

Keywords: Material selection, Supercritical reactor, Non-catalytic biodiesel

Introduction

The supercritical technique looks into an alternative to the traditional method of producing biodiesel in which usually catalyst is used. Due to the procedures involved in feedstock preprocessing, product separation, and purification, catalytic biodiesel production requires a lot of time and energy. Pre-processing and post-processing steps might be facilitated by non-catalytic biodiesel synthesis using supercritical fluid. A supercritical fluid is one of the alternatives recommended for addressing the fundamental issues in the development of catalytic biodiesel processing (Nematian et al., 2021). The working fluid is categorized as a supercritical fluid if the reaction conditions are higher than the critical temperature (T_c) and pressure (P_c) of the fluid. Compared to catalytic biodiesel production, the use of supercritical alcohol as a solvent for biodiesel manufacture is a simple method (Saka & Kusdiana, 2001; Demirbas, 2006). High pressures (>5 MPa) and high temperatures (>200 °C) can be used in the supercritical technique to produce a homogenous phase between the supercritical alcohol and the triglycerides (Al-Shanableh, 2017).

The supercritical reaction could occur without the use of a catalyst because no need for limitations in the feedstock used, such as free fatty acid and water content. Also, separating the biodiesel from the glycerol is easier because fewer discrete processes, such as catalyst purification, are needed (Sharma & Singh, 2009).

Diasakou et al. in 1998 developed non-catalytic transesterification using subcritical methanol at temperatures of 240°C, 220°C, and 235°C to overcome these drawbacks. In 2001, Saka and Kusdiana successfully produced the first biodiesel by supercritical methanol from rapeseed oil at 350°C and 45 MPa in a 5 mL-Inconel 625 batch type of reactor. Later, many other researchers investigated supercritical methanol for biodiesel production at various temperatures and pressures with various reactor sizes, and they also achieved high conversion in a short time (Pinnarat & Savage, 2010; Silva & Oliveria, 2014). In previous studies, the maximum operating pressure and temperature and reactor size were 45 MPa and 350°C (Saka & Kushidiana, 2001), the maximum reactor size was 200 mL (He et al., 2007), while the minimum values were 10 MPa, 270°C (Lee et al., 2012) and 5 mL (Saka & Kushidiana, 2001) respectively. In all these studies, the reactor with the largest volume has 200 mL, but this volume is often insufficient in terms of seeing the difficulties that may be experienced in the production of commercial biodiesel.

The aim of this study is the material selection for a bench-scale reactor that meets the operating conditions of supercritical methanol. The reactor could be scaled up to a larger size after it was designed and built on a bench scale. The investigation of problems encountered during the construction and operation of the bench-scale reactor will facilitate large-scale biodiesel production.

Supercritical Reactor for Biodiesel Production

The reactor design for supercritical processes can have a significant impact on productivity and resource consumption. The pilot plant or bench scale is preferred in many laboratory batch processes due to its low risk and ease of setup (Qadeer et al., 2021). Before designing a bench-scale-batch-type supercritical reactor, four parameters must be determined; operating pressure and temperature, reactor dimension, and materials of construction. The minimum operating pressure is 7.86 MPa (1140 psi), which is the methanol critical pressure, as shown in Figure 1, while the maximum operating pressure that could be applied was 45 MPa (Ebert, 2008). The design pressure should be 5–10% higher than the maximum operating pressure (Moss, 2004). Because design pressure is used to assign the most severe conditions, 47 MPa was chosen. The maximum operating pressure is the most important parameter in a reactor design because it is the basis for the majority of calculations, such as the nominal thickness of the reactor. The operating temperature could range from 240°C (the critical temperature of methanol) to 350°C. Temperature is an important design parameter; in particular, high temperatures are associated with thermal expansion and corrosion; therefore, material selection should be focused on the operating temperature. For evaluating the size of the reactor amount of biodiesel produced was questioned in the first place. The tests for quality evaluation required a minimum of 100 mL of the final product for each batch (Evcil et al., 2018; Al-Shanableh et al., 2019). The methanol used in biodiesel production by the supercritical method is very high, with a 1:40 oil-to-alcohol mole ratio (that corresponds to approximately 1:2 oil-to-alcohol volume ratio). To be able to produce 100 mL of biodiesel as the end product, the reactor size should be at least 600 mL which was going to hold 175 mL triglyceride and 325 mL methanol as raw materials. The last step was the material selection process and it is presented detailed in the methodology section.

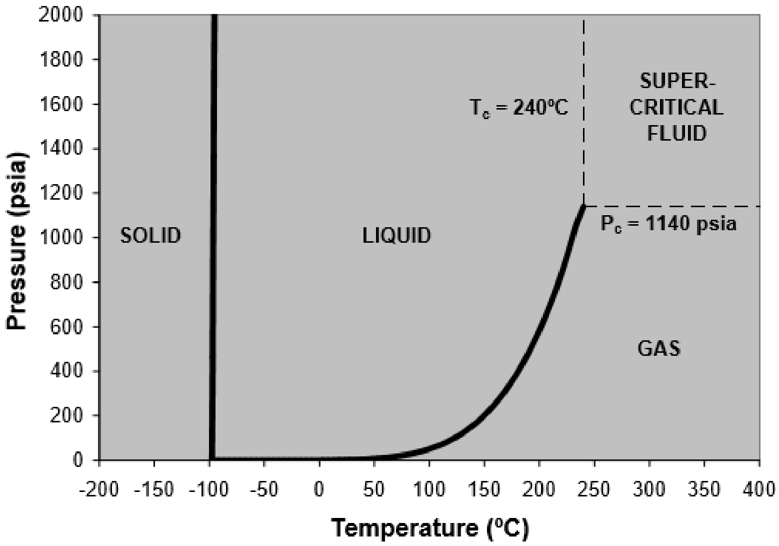

Figure 1. Phase diagram of methanol

Method

Material Selection for Supercritical Reactor

Choosing materials entails attempting to find the best match between design requirements and the properties of the materials that may be used to create the design. In the present study, Ashby's approach was followed for the material selection process that involves three steps; the definition of the problem statement, the translation that identifies material indices, and the last step is the screening and ranking, by which a full menu of materials is reduced to a shortlist (Ashby, 2011). The problem statement was to design a supercritical reactor that should be able to withstand a minimum stress of 47 MPa and a temperature of 400°C.

The most crucial design factor for a safe operation is the mechanical strength of the selected material for pressure vessels. Pressure vessels are typically built to yield at a pressure that is still too low to allow any cracks they may contain to spread ("yield before break"). To identify the stress-σ- in the wall of a spherical pressure vessel of radius R_i Equation 1 could be used;

$$\sigma = \frac{pR_i}{2t} \qquad \text{Eqn.1}$$

where t is the thickness of the vessel. According to the ASME Section VIII, Division 1, paragraph UG27, wall thickness of high pressure vessel should be $t > 0.5\ R_i$, then maximum σ will be 47 MPa and also minimum σ_f (yield stress) will be 47 MPa. Then wall thickness t,

$$t \geq \frac{pR_i}{2\sigma_f} \qquad \text{Eqn.2}$$

In a small pressure vessel if flaw is observed that should not have a diameter greater than a_c^*; then, the stress required for the crack propagate is given below;

$$\sigma = \frac{CK_{1C}}{\sqrt{\pi a_c^*}} \qquad \text{Eqn.3}$$

where C is a constant near unity, a_c^* is half of the flaw length and K_{1C} is the plane-strain fracture toughness of the material. Combination of Equations 2 and 3 gives Equation 4 that indicates the largest pressure is carried by the material with the greatest value of K_{1C}.

$$p \leq \frac{2t}{R}\frac{K_{1C}}{\sqrt{\pi a_c^*}} \qquad \text{Eqn.4}$$

A requirement that the crack is not spread even if the force surpasses the material's yield strength could increase safety. This condition is expressed by setting σ equal to the yield stress σ_y as shown in Equation 4.5,

$$\pi a_c \leq C^2\left[\frac{K_{1C}}{\sigma_f}\right]^2 \qquad \text{Eqn.5}$$

The tolerable crack size a_c, is maximized by selecting a material with the highest value of K_{1C}/σ_f, which is the criterion that meets the "yield before break". Figure 2 (Ashby, 2005) depicts the material selection criterion for safe design against fracture. Two material indices were developed;

i. $M_1 = \sigma_f > 47$ MPa
ii. The largest K_{1C}/σ_f; $M_2 = K_{1C}/\sigma_f$

Materials with equivalent performance are connected by a diagonal line with constant value $M_2 = K_{1C}/\sigma_f$; materials performing better are those above the line. Aluminum alloys are disqualified due to the first criterion however stainless steels, nickel alloys, copper, and copper alloys are all appropriate materials for the yield-before-break criteria. Other design factors such as maximum service temperature, corrosion resistance, and cost need to be considered in order to select the best material among these contenders. Out of these materials, only the steels (low alloy & stainless) and nickel alloys remain as an option, once the maximum service temperature was considered as 400°C (Ashby, 2011).

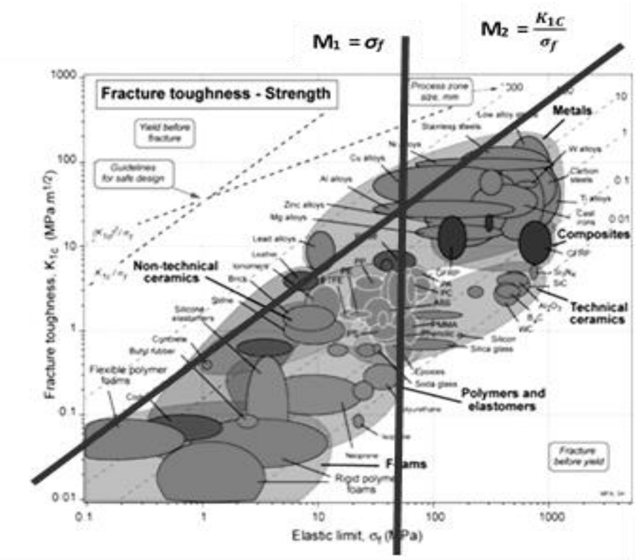

Figure 2. Material selection chart- fracture toughness, K_{1C} against strength, σ_f

Transesterification reaction involves alcohols and triglycerides that are a mixture of fatty acids so the corrosion resistance of some common metal alloys is shown in Table 1 (Peters and Timmerhaus, 2003). Stainless steel (Grade 304 and 316), nickel alloys, and copper alloys except for red brass seemed possible candidates.

Table 1. The corrosion resistance of candidate materials

Chemical	Iron and steel	Stainless steel Grade 304	Stainless steel Grade 316	Nickel (Inconel™)	Copper (Monel™)	Red brass
Fatty acids	C	A	A	A	A	C
Methanol	A	A	A	A	A	A
Oleic acid	C	A	A	A	A	C
Glycerol	A	A	A	A	A	A
Methyl esters	C	A	A	A	A	C

A= acceptable, can be used successfully, C= caution, resistance varies widely depending on conditions

Both stainless steels and nickel alloys possessed the necessary qualities: non-magnetic, corrosion resistant, and can be worked into a cylindrical vessel from a single block. Figure 3 shows the average cost difference (30 $/kg for Ni alloys vs. 7 $/kg only for stainless steels) (Ashby, 2011)

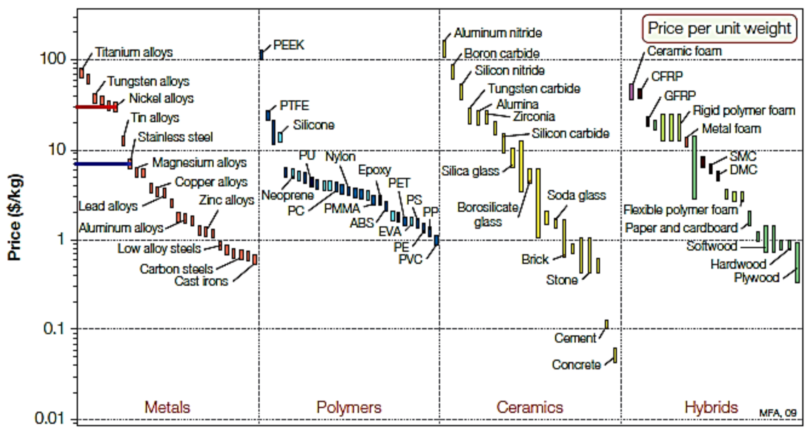

Figure 3. The approximate price/kg of materials

Results and Discussion

Materials used in the construction of high pressure vessels must meet strength, temperature, and corrosion resistance requirements, besides availability, cost, and ease of fabrication are other factors during material selection. Stainless steels, such as Grade 304 and Grade 316, and metal alloys with higher chromium, nickel, and/or molybdenum content, such as Incoloy™, Inconel™, and Hastelloy™ are the most common and widely used construction materials for pressure vessels due to their high mechanical strength, excellent corrosion resistance and stiffness (Al-Shanableh, 2017).

In the present study, it was determined that the best material for the reactor that was intended to be built for the manufacture of supercritical biodiesel was 316 stainless steel. While Grade 304 is the standard "18/8" stainless steel with excellent welding and forming properties, Grade 316 is the standard molybdenum-bearing grade with better overall corrosion-resistant properties. Besides Grade 316, with higher nickel content is considered the "most non-magnetic" stainless steel. However, 316 stainless steel with an appropriate amount of welding may be sufficiently magnetic. Since the intent of the project was to fabricate the reactor from a single piece of material without welding, Grade 316 would be a suitable option. Although, nickel-rich alloys are suitable for high pressure vessels due to their excellent corrosion resistance and stiffness, stainless steels are preferred over due to their low cost and availability. Some material properties of 316 stainless steel are shown in Table 2 (from ASME Section VIII, Div. 2, Table AMG-1 and AMG-2).

Table 2.Material properties of stainless steel-Grade 316

Properties	
Chemical Composition	Fe; < 0.03 C; 16-18.5 Cr; 10-14 Ni; 2-3 Mo; < 2 Mn; < 1 Si; < 0.045 P; < 0.03 S
Young' Modulus	205 GPa
Elastic Limit (σ_f)	310 MPa
Poison's Ratio	0.275
Ductility	0.51
Tensile Strength	620 MPa
Maximum Allowable Working Stress (*S*)	117 MPa
Fracture Toughness	278 MPa.m$^{1/2}$
Maximum Service Temperature	1198 K
Minimum Specified Yield Strength (σ_y)	at 200°C: 160 MPa at 300°C: 136 MPa at 400°C: 123 MPa

Tümtes Company, Istanbul, Turkey, manufactured the reactor by drilling and grinding a single cylindrical block of 316 stainless steel to give it the desired shape (no welding). Figure 4 depicts the plain reactor that was built (without equipment or accessories). It was critical to assess the reactor's functionality and safety before beginning any experimental research. A hydrostatic test was conducted at 90°C and 120 bar for one hour. The hydrostatic test was successfully completed by the intended supercritical reactor without showing even a minor damage.

Figure 4. Fabricated vessel with hatch and clamps

Conclusion

In order to design and fabricate a reactor for biodiesel production under supercritical methanol conditions, the material selection of the reactor was investigated in the present study. The selected material should have specifications to fulfill the task expected for the design requirements. 316 stainless steel was found to be the best choice of material for the reactor planned to be designed for supercritical biodiesel production. The reactor made up of Grade 316 stainless steel satisfies all requirements; withstands minimum stress of 47 MPa and a temperature of 400°C, offers vastly superior corrosion resistance, is not affected by the magnetic field, is relatively cost-effective, and is easy to shape into a cylindrical vessel without the need for welding. The reactor is manufactured from a single piece of cylindrical solid Grade 316 stainless steel and has passed all safety tests before it reaches the production stage.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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