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Review of Three Methods for Biodiesel Formation

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Abstract: Biodiesel is a renewable energy source. It helps reduce dependence on traditional fossil fuels and reduces the risk of energy supply. This paper compares three different ways to make biodiesel: transesterification (involving acidic, enzymatic, and basic catalysis), pyrolysis, and hydro-treatment, respectively. The methodology it used was literature searching in publications and calculating the "PMI" of these different methods to compare their advantages, disadvantages, and efficiency. The PMI (process mass intensity) is used to benchmark the "greenness" of a process by focusing on the total mass of materials used to produce a given mass of product. The results of this research come from a bunch of perspectives. The ease of separating FFA and the reduced energy intensity are among the advantages of employing transesterification techniques. The ease of separating FFA and the reduced energy intensity are among the advantages of employing transesterification techniques.

Keywords: biodiesel, PMI, transesterification, pyrolysis, hydro-treatment.

1. Introduction

Because of China's decline in fossil fuels, experts are willing to look for a substitute for petrochemicals. Besides, China's large and medium cities create 5 million tons of WCO annually, and 40%–60% of WCO illegally returns to the dining table via several routes [1]. The rest of WCO is also inappropriately treated, which causes vast environmental and health issues. Biodiesel is a renewable clean fuel made from waste vegetable oils and animal fats through chemical technology (ester exchange, pyrolysis, hydroprocessing). It can improve energy security, circular economy, and waste utilization, so it is becoming more and more popular. Therefore, the benefits of biodiesel have set off a new round of research boom around the world. And the review turns to study, reveal the particulars, and compare the differences between these three chemical techniques. First, this study will focus on analyzing the advantages and disadvantages of the three methods for producing biodiesel in order to make a preliminary and overall comparison between them. Second, this paper will calculate specific data and draw charts for comparison. In addition, the method adopted in this paper is through conducting literature research and calculating PMI. This study fills the gap regarding better chemical technology options.

2. Generally comparing

This chapter will conduct a comparative analysis from an overall perspective.

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Transesterification is a catalyzed process that transforms one ester into another ester by exchanging the R-organic group from one ester with the R′-organic group from alcohol with the aid of a solvent [1]. The method for producing the biodiesel with.

Transesterification is to add the catalyst to the waste cooking oil and the glycerin, then the transesterification will take place and the biodiesel will be formed.

And the process of biodiesel, which uses transesterification, can be divided into three parts: acidic, enzymatic, and basic catalysis.

Pyrolysis could be one of the most simple methods for producing biodiesel. Because, compared with transesterification, pyrolysis only requires putting the waste cooking oil at a high temperature to break the bonds and produce biodiesel. But it needs too much energy.

The hydrotreating process mainly involves deoxygenating waste cooking oil, which can improve stability and environmental friendliness.

Table 1: generally comparing

	Reaction Type	Example	Pros	Cons
Acidic	Esterification Transesterification	H_2SO_4 (high P and high T)	Easy to separate FFA	Slow Large catalyst loading Corrosion problems
Basic (alkaline catalysis)	Transesterification Esterification	NaOH (25-40°C) and KOH	Cheap Fast	Be likely to form the soap
Enzymatic (need pretreatment to deal with FFA)	Transesterification Esterification	Lipase	Mild reaction conditions No pollutants Lower E use	High cost Short life span Need extremely stable conditions
Hydrotreatment	Hydro deoxygenated		Lower acidity High stability Renewable	Expensive
Pyrolysis (do not need catalyst)	Cracking	SCA	Low demand of feedstock	Energy intensive

Table 1 has indicated the information which are collected on the publication. It involved the benefits, disadvantages, examples and also the reaction types of different methods that produce the biodiesel.

Table 1 completely provided the information that can be used to do the compiling. It can be seen that the acidic one can easily separate FFA (fatty-free acids) [2], which are seen as waste during the reaction. However, the reaction speed will be slow while using an acidic catalyst, and a large catalyst will be loading, so there might be some corrosion problems. By contrast, with alkaline catalysis, one can react quite quickly, but the risk is that it is likely to form soap, which is really dangerous for the environment. Besides, the enzymatic one could be so complex that it needs pretreatment to deal with

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FFA, and it costs a lot. Additionally, the enzyme needs extremely stable conditions to perform; however, the pros of using it are that the conditions they need during the reaction are mild, no pollutants will be produced, and it also needs less energy. What's more, for the hydro-treatment one, it has high stability and is a renewable resource, but it is very expensive. As for the last one—the pyrolysis—it costs only a small amount of feedstock, but it is really energy intensive.

All in all, these methods have various benefits from different perspectives.

3. PMI calculations

After the overall understanding, this chapter will conduct a comparative analysis from the perspective of PMI (Process Quality Intensity) calculation.

The PMI is a kind of special intensity that measures the "greenness" of a process [3]. PMI is the ratio of the total mass of input materials used in the process to produce 1 kg of the active pharmaceutical ingredient (API) [4]. Therefore, a lower PMI implies a more materially efficient process. Optimization of resource usage not only improves the environmental sustainability of a process, 16 and the formula for the process mass intensity is:

PMl = total input mass in a process or process step (kg) mass of active product (kg) [4]

By searching previous experiments, a large amount of data is available concerning the quality of the inputs to the process and the yield of biodiesel as a desired product. Therefore, this paper calculates the PMI for experiments on biodiesel formation through transesterification (involving acidic, enzymatic, and alkaline catalysis), pyrolysis, and hydrotreating reactions. In this case, the most efficient methods for producing biodiesel and measuring its "greenness" can be obtained.

Table 2: the result of PMI calculation

Type of oil	PMI	method	Yield
Corn oil [5]	7.2	acid	80.00%
Euphorbia lathyris L. oil [6]	1.324	acid	85.60%
Curcas L. oil[6]	1.341	acid	84.20%
Palm oil[6]	1.348	acid	91.40%
Sapindus mukorossi kernel[7]	1.72	acid	87.00%
Sapindus mukorossi kernel[6]	1.308	acid	86.30%
Waste cooking oil[8]	3.47	acid	74.30%
Bitter almond oil[9]	5.39	alkaline	88.40%
Euphorbia lathyris L. oil[6]	1.363	alkaline	86.20%
J. curcas L. oil[6]	1.366	alkaline	86.20%
soybean oil [10]	1.47	alkaline	93.00%
ss kernel oil[6]	1.333	alkaline	88.30%
Waste cooking oil[11]	1.58	alkaline	95.78%
Palm oil [12]	1.58	enzyme	97.90%
Rubber oil[13]	5.59	enzyme	23.22%
Waste cooking oil[12]	1.23	enzyme	98.14%
Rubber oil[14]	1.4	enzyme	92.83%
soybean oil[15]	1.193	hydrogenation	79.00%
Beef fat	1.21	pyrolysis	82.78%
soybean oil	1.39	hydrogenation	74.80%

Table 2 shows all the PMI this study calculated.

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As the table shows, almost all the values of PMI we calculated are in the range of 1 to 2, while there are some large values. The major causes are various, including a large number of catalysts and excessively repeated washing steps for biodiesel purification.

The yellow area shows a yield of 80%~90%, and the green one shows the yield of more than 90%. In addition, the red area shows a yield that is below 80%.

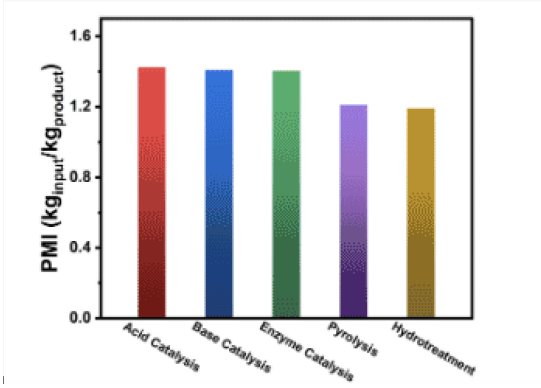


Figure 1: average PMI of different methods

Figure 1 shows that the average PMI value for biodiesel produced using acidic, alkaline or enzymatic catalysis is about 1.4 kg input/kg product. Pyrolysis and hydroprocessing have a PMI of about 1.2 kg input/kg product. Nevertheless, when glycerol is further used as a byproduct of biodiesel production, it is possible to reduce the PMI value of biodiesel produced using acidic, alkaline or enzymatic catalysis by 12%. In this case, it can be seen that transesterification, pyrolysis and hydroprocessing can show similar resource utilization. However, pyrolysis and hydroprocessing of WCO (waste cooking oil) are more expensive and energy-intensive processes than WCO (waste cooking oil) transesterification.

4. Conclusion

In sum, this study focuses on different methods of forming the biodiesel and compares the advantages and also the disadvantages of them. We evaluated them by searching literature information and determining the PMI values. The PMI values for WCO pyrolysis and hydro-treatment are lower than those for biodiesel production via Transesterification using acid, alkaline or enzyme catalysts. However, pyrolysis and hydro-treatment are more expensive to implement on an industrial scale. In addition, pyrolysis and hydro-treatment of WCO are more energy intense compared to (trans) esterification. Therefore, Transesterification of WCO is still a more interesting process route for the production of biodiesel when the purification steps are optimized to utilize less materials.

And this researching is limited by only doing it by literately searching, which means the results of this article might not totally accurate. In addition, the calculations seems not enough for evaluating, thus the results might be not that rigorous.

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