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Internal mass-transfer limitations on the transesterification of coconut oil using an anionic ion exchange resin in a packed bed reactor

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ABSTRACT

In this study, a strongly basic anion-exchange resin was used for the transesterification of coconut oil and methanol using a continuous-flow packed-bed reactor. Statistical analysis shows that the observed conversion and apparent bulk reaction rate are insensitive to temperature. This suggests that mass transfer is the rate-determining step. Analysis of the Wagner–Weisz–Wheeler (WWW) modulus shows that the observed reaction rate is strongly influenced by internal mass-transfer resistances (WWW > 4) under most of the experimental conditions used. However, in some tests, the overall reaction rate can be said to be in the transition regime between reaction control and internal mass-transfer control (0.15 < WWW < 4). Extended continuous flow experiments showed no noticeable decline in the catalyst activity even after almost 400 reactor bed void volumes of biodiesel had been produced. These results suggest that the catalyst and thus the overall reactor performance may be further improved by increasing the porosity.

1. Introduction

Biodiesel has been increasingly recognized as a viable, immediately available alternative to petroleum-derived diesel fuel but universal acceptance of biodiesel has been hampered by high costs and limited availability of feedstock [1]. The traditional process for manufacturing biodiesel uses NaOH (or other soluble bases like KOH) as the catalyst for the transesterification reaction. While NaOH is an adequate catalyst for traditional feedstocks, many of the newly proposed alternative feedstocks, including used cooking oil, are known to have a high amount of free fatty acids which react with the catalyst to form soaps, thereby reducing yield and hindering separation of the biodiesel from the byproduct glycerin [2]. Soap is considered to be an impurity and is removed from the biodiesel by washing with water. If the washing step can be reduced or eliminated, a considerable savings in cost and resources could be realized.

To address this need, several approaches have been used, one of which is to use heterogeneous catalysts to catalyze the transesterification reaction. The use of heterogeneous catalysts for the transesterification reaction was reviewed recently [3–7].

Ion-exchange resins, either in cationic form [8–15] or in anionic form [16–19] have been proposed as a means for catalyzing the transesterification. Shibasaki-Kitakawa et al. [18] made use of triolein as the triglyceride to test a variety of ion-exchange resin catalysts. It was found that reaction rates are higher with porous-type resins (PA 308, PA 306 and PA 306s) as catalysts than with the highly porous-type resin (HPA 25). It was noted that the resin with the lowest cross-linking density and smallest particle size gave the highest reaction rate. During the experiments run at 50 °C, it was also found that the optimum oil-to-alcohol molar ratio is 1:6, and resins could be used repeatedly without loss in catalytic activity. Marchetti et al. [17] studied the esterification of free fatty acids using two anionic ion-exchange resins. One of their key findings was that the reaction rate was insensitive to the temperature and, in fact, that the reaction rate was highest at the lowest temperature.

In this work, we report on experiments done on a strongly basic anionic ion-exchange resin in a packed bed reactor and observe possible influences of mass-transfer on the overall reaction rate.

2. Materials and methods

Fig. 1 shows the reactor system for the continuous flow experiments, which is similar to that used by Shibasaki-Kitakawa et al. [18]. To avoid separation of phases in the reactor and to hold the catalyst, silica wool was put on top of the catalysts. The dimensions of the silica glass reactor are also shown in Fig. 1. The feed consists of refined, bleached and deodorized coconut oil and methanol

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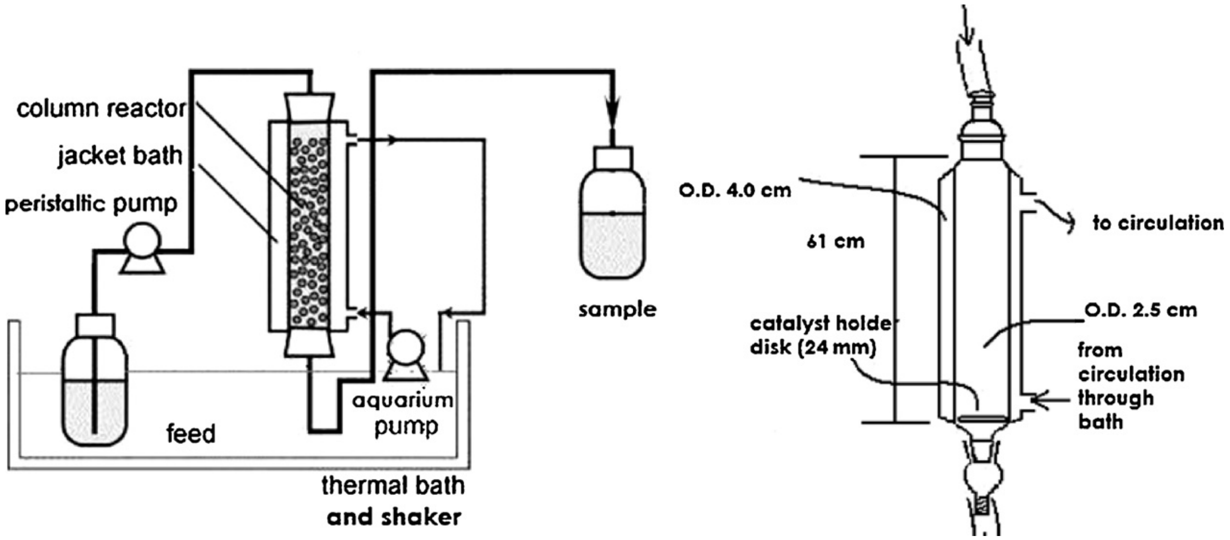

Fig. 1. Feed and temperature control system and reactor dimensions.

(AR grade, >99.8% purity, <0.1% moisture) at a fixed ratio. The coconut oil had a moisture content of 0.106% and an acid value of 0.09 mg KOH/g oil. The ion-exchange resins (Dowex Marathon MSA Type 1 strong base anion exchange resin) were supplied by Dow Chemical in the chloride form. The information sheet from the manufacturer [20] indicates that resin is macroporous, the base is Styrene-DVB and the functional group is quaternary amine. The resin was pre-treated by immersion in a saturated solution of sodium methylate in methanol. The expected swelling from the chloride to the hydroxide form is 10% [20]. The catalyst was then separated and washed with a volume of methanol roughly equivalent to the volume of the catalyst bed to wash away the excess sodium methylate that was not attached to the surface of the catalyst. The catalyst was prepared in batches and stored in methanol prior to use.

After drying in an oven for 18 h, the untreated resins were found to have an average of 45.4% dry solids content while the pre-treated resins were found to have an average of 73.9% dry solids content. By titration, the ion-exchange capacity of the treated resin was found to average 1.3 equivalents HCl per kg dry resin. Brunauer–Emmett–Teller analysis using Autosorb showed that the resin has a surface area of 0.578 m^2/g and an average pore diameter of 1.9 nm.

Experiments were conducted using two-level factorial statistical design of experiment (DOE) approach. This approach is useful for investigating linear effects of experimental factors and their interactions on experimental responses; generally the emphasis of such an approach is to establish the statistical significance of these influences, rather than to develop detailed mechanistic models [21]. This approach is justified by the relative complexity of the transesterification reaction, which involves multiple reaction and mass transfer steps, and has been applied recently to investigate biodiesel production (e.g., [15,22,23]). The experimental design is shown in Table 1. At the end of each run, the product mixture was distilled to remove unreacted methanol. The product left after distillation was transferred to a separatory funnel to separate the biodiesel phase from the glycerin phase. Biodiesel samples were analyzed for acid value, total glycerin content, water content and specific gravity by Senbel Fine Chemicals Corporation, a biodiesel company based in the Philippines.

In order to determine whether the system had achieved steady-state operation, the refractive index of the product stream was measured, since the refractive index is correlated to the composition of the reacting mixture as reported by Xie and Li [24]. A typical time-course measurement is shown in Fig. 2.

Table 1
Levels of experimental parameters used.

Run	Thermal bath temperature (°C)	Alcohol-to-oil mass ratio	Space time (h)
1	60	1:6	0.181
2	60	1:4	0.134
3	60	1:6	0.110
4	60	1:4	0.054
5	40	1:6	0.542
6	40	1:4	0.151
7	40	1:6	0.082
8	40	1:4	0.048

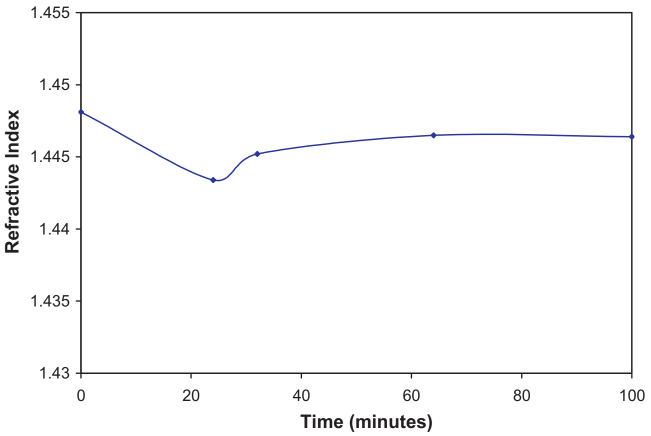

Fig. 2. Time-course experiments for Run 4.

To test the stability of the resin, a bed of pre-treated resin with a height of 3.0 cm was used to produce 2.285 kg or 2529 cm^3 of biodiesel. This volume is equivalent to 10 consecutive runs of experiments similar to those discussed in the previous section. This volume is also 383 times the void volume of the catalyst bed. It can be seen in Fig. 3 that there was no significant decline in the conversion of the reactants to biodiesel. Therefore, the results presented here can be regarded as true steady states, unaffected by leaching of residual alkali in the resin or subsequent catalyst deactivation.

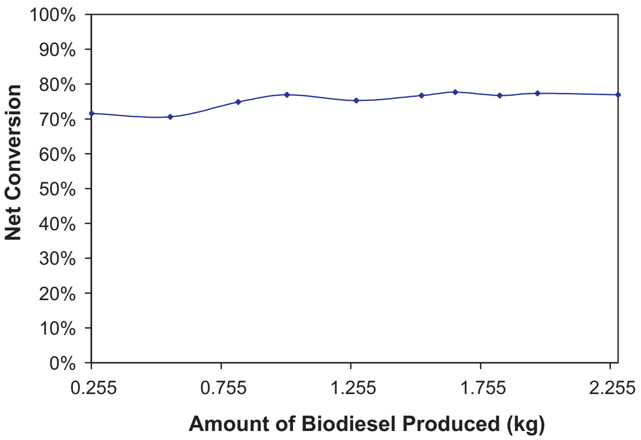

Fig. 3. Variation of conversion with the amount of biodiesel produced.

3. Results and discussion

3.1. Dependence of conversion and overall reaction rate on key parameters

Results from analysis of the distilled biodiesel layer from the flow experiments are summarized in Table 2. The conversion is computed from the total glycerin content of the biodiesel sample via Eq. (1). The computation is based on the fact that pure methyl ester contains no bound glycerin; on the other hand, the bound glycerin content the unreacted triglyceride can be found stoichiometrically from its molecular weight. Thus, a given biodiesel sample will contain less bound glycerin as more triglyceride is converted to methyl ester [25]. This approach assumes that there are no monoglycerides and diglycerides in the biodiesel sample, and hence provides a conservative estimate of conversion.

$$X = \left[\frac{m_C - m_B(x_{TG} - x_{FG})(M_C/M_G)}{m_C} \right] \times 100\% \qquad (1)$$

where X is the conversion, m_B is the mass of the biodiesel phase produced, m_C is the mass of the coconut oil fed, x_{TG} is the mass fraction of the combined amount of bound and unbound glycerin in the biodiesel phase, x_{FG} is mass fraction of the unbound glycerin in the biodiesel phase, M_C is the mean molecular weight of coconut oil and M_G is the molecular weight of the glycerin. In this equation, the term $m_B(x_{TG} - x_{FG})$ accounts for the glycerin bound to unconverted triglycerides in the biodiesel phase. When multiplied by the ratio of the molecular weight of coconut oil to the molecular weight of glycerin (M_C/M_G), the mass of unreacted coconut oil is obtained. Therefore, the numerator in Eq. (1) gives the amount of coconut oil that reacted.

Phase equilibrium data [26] indicates that the free glycerin is low in the biodiesel phase when the methanol content is low and thus if a further assumption is made that the free glycerin is negligible in the distilled biodiesel layer, then the conversion may be estimated from Eq. (2) below.

$$X = \left[\frac{m_C - m_B(x_{TG})(M_C/M_G)}{m_C} \right] \times 100\% \qquad (2)$$

An overall reaction rate may be computed by

$$r_A = \frac{\dot{N}_{A0} X}{m_{catalyst}} \qquad (3)$$

where $\dot{N}_{A0}$ is the number of moles fed in one space time, X is the conversion, and $m_{catalyst}$ is the mass of the catalyst. Here, an assumption is made that the bed is uniform and that the rate used is the aggregate bed reaction rate. This rough approximation is still useful for giving indicators on relationships between the response and the parameters. Conversion and reaction rate at each of the experimental runs are summarized in Table 2. Note that conversion levels ranging from 68.5% to 78% were achieved even with very short space times. In seven of the runs, the values ranged from 0.05 to 0.18 h. Problems were encountered with the feed pump during Run 5, leading to a space time significantly higher than the rest of the test runs; however, this run did not achieve a conversion level that was noticeably greater than the rest of the results, which suggests that reaction equilibrium was preventing further conversion of the reactants.

Analysis of variance (ANOVA) was used to determine whether each experimental parameter tested had a statistically significant

Table 2
Analysis of distilled biodiesel layer from flow experiments.

Run	Moisture (%)	Acid value (mg KOH/g)	Total glycerin (%)	Soap (ppm)	Specific gravity (25 °C)	Conversion (%)	Observed reaction rate (mol/kg-s)	Wagner–Weisz–Wheeler modulus
1	0.132	0.06	4.67	–	0.898	74.6	1.46×10^{-3}	4
2	0.186	0.05	4.78	61	0.883	74.6	4.92×10^{-3}	6
3	0.152	0.06	4.87	64	0.911	71.5	5.99×10^{-3}	7
4	0.197	0.07	4.79	24	0.914	71.5	1.12×10^{-2}	4
5	0.188	0.07	4.70	94	0.912	72.1	1.16×10^{-3}	2
6	0.186	0.06	4.76	30	0.913	74.3	4.49×10^{-3}	5
7	0.159	0.06	4.66	30	0.882	68.5	4.46×10^{-3}	3
8	0.193	0.06	4.77	15	0.913	73.0	1.17×10^{-2}	10
9[a]	0.130	0.10	3.48	77	0.901	78.0	3.42×10^{-3}	7

[a] Experiments on the long term stability of resins.

Table 3
Statistical analysis of the influence of experimental parameters on conversion and apparent reaction rate.

Parameters	Conversion			Apparent reaction rate		
	Direction of effect	*p*-Value	Significance	Direction of effect	*p*-Value	Significance
Thermal bath temperature	+	0.576	○	+	0.952	○
Methanol to oil mass ratio	–	0.083	*	+	0.641	○
Space time	+	0.069	*	+	0.511	○

*, statistically significant effect at $\alpha = 10\%$.
○, statistically insignificant effect at $\alpha = 10\%$.

effect on the conversion. The statistical significance of an observed effect can be determined by computing the p-value. Generally, p-values are compared to a predefined level of significance (α); an experimental parameter is considered as statistically insignificant if its p-value > α. In this work, we use $\alpha = 0.10$ which corresponds to a 90% confidence level. For the statistical analysis, we excluded the results of Run 5, during which feeding problems were encountered, as explained above. Table 3 summarizes the results of the statistical analysis. As may be expected, the space time has a statistically significant positive effect on conversion. Also expected is the observation that the space time has no statistically significant effect on the apparent reaction rate. The methanol–oil mass ratio has a statistically significant *negative* effect on conversion. This counterintuitive result hints at a substrate inhibition effect, which may be explained as follows. A large methanol excess in the bulk phase results in an even larger excess at the catalyst surface, since the lighter alcohol molecules are able to diffuse through the pores more readily than the heavy triglyceride molecules. The excess methanol thus inhibits the triglyceride concentration at the catalytic site. Although this causes a local forward shift in the reaction equilibrium that then results in high conversion levels, this effect is localized at the catalyst surface only. The overall conversion in the bulk phase is reduced, as the small quantity of methyl ester product released from the catalyst surface is subsequently diluted by the unreacted triglyceride. An alternative hypothesis would be the dilution effect on the limiting reactant (coconut oil) and, therefore, there is a lower driving force for both diffusion and reaction. However, there is insufficient data in the analysis of the dependence of reaction rate on methanol–oil ratio to confirm either hypothesis. This effect should be studied further.

The most important observation from the statistical analysis is the observation that temperature has no statistically significant effect on either conversion or apparent reaction rate. This suggests that the overall reaction may be controlled by internal mass transfer. This hypothesis is further tested in the next section.

3.2. Calculation of the Wagner–Weisz–Wheeler modulus

When a porous catalyst such as an ion-exchange resin is used, the reactant must diffuse to and through the catalyst particle in processes called inter- and intra-particle diffusion, respectively, before it can react with the active catalyst surface. The extent of the influence of internal and external mass transfer on the overall reaction rate can be estimated by using the Wagner–Weisz–Wheeler modulus

$$M_W = L^2 \frac{(-r'''_A/C_A)_{\text{observed}}}{D_{\text{effective}}} \tag{4}$$

where $D_{\text{effective}}$ is the effective diffusion coefficient of the fluid in the porous structure, L is the characteristic size of the catalyst particle equal to the quotient of the volume of the particle and the exterior surface available for reactant penetration, $-r'''_A$ is the observed reaction rate and C_A is the concentration of the reactant [27]. When the reactant fully penetrates the particle and bathes all its surfaces, the Wagner–Weisz–Wheeler modulus is below 0.15 and the particle is in the diffusion free regime. On the other hand, when the center of the catalyst particle is not reached by the reactant or is unused, the particle is in the strong pore resistance regime which occurs when the Wagner–Weisz–Wheeler modulus are above 4.

To calculate the Wagner–Weisz–Wheeler modulus, $C_{39}H_{71}O_6$ was used as an approximate molecular formula for coconut oil triglyceride.

$$V = \sum (\text{Atomic volume})(\text{No. of elements in compound}) \tag{5}$$

Eq. (5) gives 9.06×10^{-4} m^3/mol and 3.70×10^{-5} m^3/mol as the molecular volumes of the triglyceride and the methanol, respectively. Eq. (6) [28] is used to calculate liquid diffusion of coconut oil at infinite dilution in methanol.

$$\frac{D_{AB}\mu_{\text{Methanol}}}{T} = \frac{7.4 \times 10^{-8}(\Phi_{\text{Methanol}} M_{\text{Methanol}})^{0.5}}{V^{0.6}_{\text{Coconut Oil}}} \tag{6}$$

where $\Phi_{\text{Methanol}} = 1.9$ is the association parameter for methanol, M_{Methanol} is the molecular weight of methanol, $\mu_{\text{Methanol}} = 3.3 \times 10^{-4}$ kg/(m s) is the viscosity of methanol taken at $T = 333.15$ K for a conservative estimate, to obtain a diffusivity D_{AB} of 9.8×10^{-10} m^2/s. In the same manner, the liquid diffusion at infinite dilution of methanol in coconut oil was obtained as $D_{AB} = 1.2 \times 10^{-9}$ m^2/s. For concentrated solutions containing an associating compound such as methanol, the correlation proposed by Leffler and Cullinan can be used to estimate the diffusivity [28]:

$$D_{AB}\mu = (D_{AB}\mu_B)^{x_B}(D_{BA}\mu_A)^{x_A} \tag{7}$$

where x_A and x_B are the molar fractions of coconut oil and methanol, respectively, and μ_A and μ_B are the viscosities of the coconut oil and the methanol, respectively. A conservative diffusivity value of 1.1×10^{-9} m^2/s which could be used for the estimation of the pore diffusivity is obtained.

The reduced pore diameter φ can be calculated by the equation

$$\varphi = \frac{d_s}{d_p} \tag{8}$$

where $d_s = 1.4 \times 10^{-9}$ is the estimated diameter of the molecule and $d_p = 1.9 \times 10^{-9}$ m is the pore diameter. The reduced pore diameter of 0.7345 is then used to calculate the two diffusivity correction factors $F_1(\varphi)$ and $F_2(\varphi)$ [28] as follows:

$$F_1(\varphi) = (1 - \varphi)^2 = 0.07049 \tag{9}$$

$$F_2(\varphi) = 1 - 2.104\varphi + 2.09\varphi^3 - 0.95\varphi^5 = 0.080 \tag{10}$$

Using these, the effective pore diffusion is calculated as

$$D_{\text{effective}} = D_{AB}F_1(\varphi)F_2(\varphi) = 6.0 \times 10^{-12} \quad \text{m}^2/\text{s} \tag{11}$$

Taking the characteristic size of the catalyst as 1×10^{-4} m, the lower limit of the particle size indicated manufacturer's information sheet [20], the WWW modulus at each of the experimental runs is determined. The results are summarized in Table 2. The values computed range from 2 to 10. Many of the runs showed that the observed reaction rate is strongly influenced by internal mass-transfer resistance (WWW > 4). In the others, the overall reaction rate can be said to be in the transition regime between reaction control and internal mass-transfer control (0.15 < WWW < 4). This is consistent with the observation that the system does not show any sensitivity to temperature. Also, it can be seen in Fig. 4 that, in general, a lower space time results in a higher WWW modulus, but the correlation coefficient is not particularly strong ($R = -0.34$). In other words, when the reaction mixture passes through the catalyst bed at a faster rate, the influence of pore resistance is greater. The reaction spends less time in the catalyst bed and has less time to penetrate into the catalyst particle.

Since the smallest particle diameter of the catalyst was used, then the estimate of the WWW modulus may be considered to be low and thus it is likely that the overall reaction is mass-transfer controlled. There are important implications if the overall reaction is indeed internal diffusion controlled. Since the overall reaction rate is largely independent of fluid velocity and temperature, there is little that can be done in terms of changing reaction conditions that may be constrained by other operational considerations. Improvements can be achieved solely by modifying the characteristics of the MSA catalyst such that internal diffusion is improved. This can be done simply by increasing the porosity or decreasing

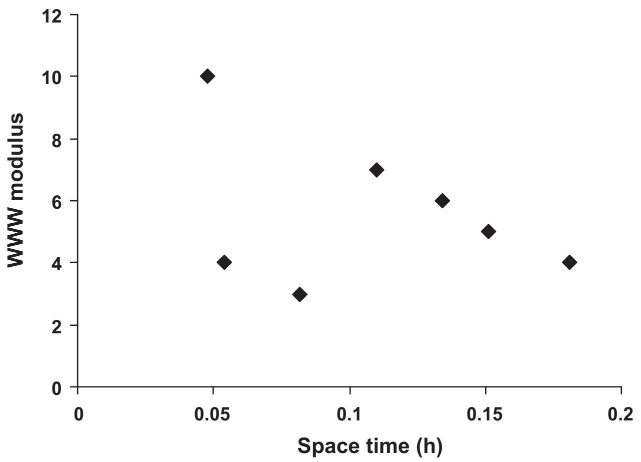

Fig. 4. Variation of the WWW modulus with space time.

the particle size further, although a higher pressure drop may be the consequence of the latter.

4. Conclusions

Two key observations are consistent with the hypothesis that the overall reaction-rate is internal mass-transfer controlled: the insensitivity of the conversion and the apparent reaction rate to the temperature and the relatively high values of the Wagner–Weisz–Wheeler modulus. To our knowledge, other studies on the use of ion-exchange resins for transesterification have not considered this possibility. The hypothesis makes sense because the triglyceride molecule is very large and branched and, since methanol is insoluble in the vegetable oil, this is essentially a three-phase system. The observation of Shibasaki-Kitakawa et al. [18] that the ion-exchange resin with the smallest particle size and the lowest cross-linking density gave the highest activity is consistent with this hypothesis. The observation of Marchetti et al. [17] that the reaction rate is not affected by the temperature is also consistent with this hypothesis. Future studies with ion exchange resins must consider the possibility of mass-transfer control before reaction mechanisms may be proposed.

A further comment may be made that this resin showed good activity and yielded very good quality biodiesel and glycerin. Further studies to improve the catalyst and elucidate the reaction mechanism would be well worth the effort. Also, the effect of impurities such as free fatty acids on the life of the catalyst should be assessed. A high free fatty acid oil can also be pretreated using anionic ion exchange resins [12,29].

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