

The Effects of Using Bio-diesel as Fuel on Compression Ignition (CI) Engine and Its Production from Vegetable Oils

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Abstract. This study presents an experimental investigation into the effects of using bio-diesel blends on diesel engine performance and its emissions. The bio-diesel fuels were produced from vegetable oils using the transesterification process with low molecular weight alcohols and sodium hydroxide then tested on a steady state engine test rig using a Euro 4 four cylinder Compression Ignition (CI) engine. Production optimization was achieved by changing the variables which included methanol/oil molar ratio, NaOH catalyst concentration, reaction time, reaction temperature, and rate of mixing to maximize bio-diesel yield. The technique used was the response surface methodology. In addition, a second-order model was developed to predict the bio-diesel yield if the production criteria is known. The model was validated using additional experimental testing.

Keywords: vegetable oil, biodiesel, exhaust gas emissions, engine performance.

1. Introduction

Bio-fuels are the fuels produced from renewable resources, particularly plant derived materials. There are mainly two types of bio-fuels (first generation): ethanol – produced by fermentation of starch or sugar (e.g., grains, sugarcane, sugar-beet, etc.) and bio-diesel – produced by processing vegetable oils (e.g., sunflower, rapeseed, palm-oil, etc.). Another type of bio-fuel is cellulosic ethanol known as second generation, is produced mainly from wood, grasses and other lignocellulosic materials from renewable sources. Bio-fuels have become a high priority in the European Union, Brazil, the United States and many other countries, due to concerns about oil dependence and interest in reducing greenhouse gas emissions. The European Union Bio-fuels Directive required that member states realize a 10% share of bio-fuels (on energy basis) in the liquid fuels market by 2020 [1]. For bio-diesel production, most of the European countries use rapeseed and sunflower oil as their main feedstock, soybean oil is the main feedstock in the United States. Palm oil in South-east Asia (Malaysia and Indonesia) and coconut oil in the Philippines are being considered. In addition, some species of plants yielding non-edible oils, e.g. jatropha, karanja and pongamia may play a significant role in providing resources. Bio-diesel is derived from vegetable oils or animal fats through transesterification process [2] which uses alcohols in the presence of a catalyst that chemically breaks the molecules of triglycerides into alkyl esters as bio-diesel fuels with glycerol as a by-product. The commonly used alcohols for the transesterification include methanol and ethanol. Methanol adopted most frequently, due to its low cost. Engine performance testing of bio-diesel is indispensable for evaluating its relevant properties. Several research groups have investigated the properties of a bio-diesel from soybean oil in diesel engines and found that particulate matter (PM), CO, and soot mass emissions decreased, while NO_x increased. Labeckas and Slavinskas [3], examined the performance and exhaust emissions of rapeseed oil methyl esters in direct injection diesel engines, and found that there were lower emissions of CO, CO₂ and HC. Similar results were reported by Kalligeros et al. [4], for methyl esters of sunflower oil and olive oil when they were blended with marine diesel and tested in a stationary diesel engine. The objectives of this study are that the vegetable oil bio-diesel produced in the laboratory improved the engine performance and

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reduced exhaust gas emissions with a stability acceptable according to ASTM D6751 (which was correlated to the content of pigments such as gossypol) [5]. In addition, this study was evaluated the suitability of Response Surface Methodology for optimizing the methanolysis of vegetable oil, including the development of a mathematical model describing the relationships and subsequent effects of the primary process variables.

2. Materials and Methods

2.1. Materials

Methanol and sodium hydroxide were purchased from Fisher Scientific (Loughborough, Leicestershire, UK). Pure vegetable oils were bought from local shops in Huddersfield, United Kingdom. Waste cooking oil was supplied by Huddersfield University Catering Services.

2.2. Fatty acid profile

3 mg of oil was weighed and mixed with 50 ml of ethanol. The mixture of oil and alcohol was heated on a hotplate, until almost boiling. At this stage 3 drops of phenolphthalein were added to the mixture as a pH indicator. Then 0.025M ethanolic NaOH was added drop by drop for transesterification, this give the solution a faint permanent pink colour. While titrating the contents of the flask was swirled by magnetic stirrer to thoroughly mix the contents. The end point of the titration was when the pink colour persisted for about 20-30 seconds.

3. Experimental Setup Design

3.1. Transesterification process

A commercial bio-diesel processor “Fuelpod” manufacturer was used for the production of bio-diesel from vegetable oils. For the transesterification process shown in Figure 1, vegetable oil was taken in a single tank section and heated at 65°C for 2-3 hours. The NaOH required for the transesterification was added to the tank as a mix of methanol. Methyl Ester forms the upper layer in the separating funnel and glycerol forms the lower layer. The machine processor which converted vegetable oil to bio-diesel in this study is a complete system used at the University of Huddersfield automotive laboratory for making bio-diesel.

3.2. Optimization process

Optimization of the transesterification process was conducted via a 3-factor experiment to examine effects of methanol/oil molar ratio (M), reaction time (T), and catalyst concentration (C) on yield of methyl ester using a central composite rotatable design (CCRD). The CCRD consisted of 20 experimental runs ($2^k + 2k + m$, where k is the number of factors and m the number of replicated centre points), eight factorial points (2^k), six axial points ($2 \times k$), and six replicated centre points ($m = 6$). Here k is the number of independent variables, and $k=3$ should provide sufficient information to allow a full second-order polynomial model. The axial point would have $\alpha = 1.68$. The centre point is the median of the range of values used: 6/1 for methanol/oil molar ratio, 1% catalyst concentration and 70 min reaction time. Table 1 shows the levels used for each factor, and to avoid bias, the 20 experimental runs were performed in random order as shown in Table 2. The experimental data presented in Table 2 was analyzed using response surface regression (RSREG) procedure in the statistic analysis system (SAS) that fits a full second-order polynomial model.

$$y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^3 \sum_{j=1}^2 \beta_{ij} x_i x_j$$

Where y is % methyl ester yield, x_i and x_j are the independent study factors, and β_0 , β_i , β_{ii} , and β_{ij} are intercept, linear, quadratic, and interaction constant coefficients, respectively.

3.3. Engine test process

The performance of the bio-diesel produced by the transesterification process was evaluated on a Euro 4 diesel engine mounted on a steady state engine test bed. The engine was a four-stroke, direct injection diesel engine, turbocharged diesel, 2009 2.2L Ford Puma Engine as used on the range of Ford Transit vans. The general specification was Bore = 89.9 mm, stroke = 94.6 mm, engine capacity = 2402 cc, compression ratio

= 17.5:1, fuel injection release pressure = 135 bar, max power = 130 kW @ 3500 rpm, max torque = 375.0 Nm @ 2000-2250. Emissions were measured using a Horiba EXSA 1500 system, measuring CO₂, CO, NO_x and THC. The test procedure was to run the engine at 25, 50, 75 and 100% engine load over a range of predetermined speeds, 1500, 2200, 2600, 3000 & 3300 rpm.

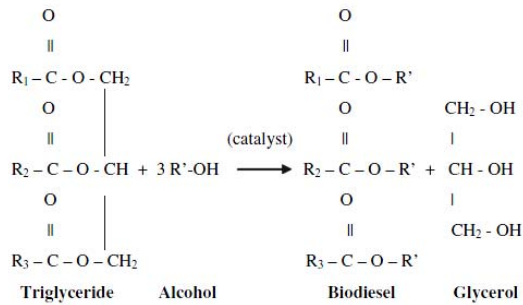


Fig. 1: Stoichiometric transesterification reaction.

Table 1: Independent variable and levels used for CCRD in methyl ester production.

Independent Variable	Symbol	Codes and Levels				
		-1.68	-1	0	1	1.68
Reaction Time (min)	(X1)T	53	60	70	80	86.8
Methanol/oil Molar Ratio (mol/mol)	(X2)M	0.95	3	6	9	11
Catalyst Concentration (wt.%)	(X3)C	0.16	0.5	1	1.5	1.8

Table 2: Central composite rotatable design arrangement and responses for methyl ester production.

Run	CCRD component	(X ₁)T (min)	(X ₂)M (mol/mol)	(X ₃)C (wt.%)	Yield (%)
1	Factorial	(-1)60	(-1)3	(-1)0.5	24.6
2	Factorial	(1)80	(-1)3	(-1)0.5	15.56
3	Factorial	(-1)60	(1)9	(-1)0.5	70.39
4	Factorial	(1)80	(1)9	(-1)0.5	88.34
5	Factorial	(-1)60	(-1)3	(1)1.5	66.61
6	Factorial	(1)80	(-1)3	(1)1.5	52.65
7	Factorial	(-1)60	(1)9	(1)1.5	86.19
8	Factorial	(1)80	(1)9	(1)1.5	98.79
9	Axial	(-1.68)53	(0)6	(0)1	92.80
10	Axial	(1.68)86.8	(0)6	(0)1	96.17
11	Axial	(0)70	(-1.68)0.95	(0)1	8.10
12	Axial	(0)70	(1.68)11	(0)1	85.77
13	Axial	(0)70	(0)6	(-1.68)0.16	30.80
14	Axial	(0)70	(0)6	(1.68)1.8	75.27
15	Center	(0)70	(0)6	(0)1	97.52
16	Center	(0)70	(0)6	(0)1	97.52
17	Center	(0)70	(0)6	(0)1	97.52
18	Center	(0)70	(0)6	(0)1	97.52
19	Center	(0)70	(0)6	(0)1	97.52
20	Center	(0)70	(0)6	(0)1	97.52

Table 3: Regression coefficients of predicted quadratic polynomial model for methyl ester production.

Terms	Coefficients	p-value
β_0	-121.52	0.0001
β_1 (time)	-1.2865	0.6891
β_2 (molar ratio)	+32.050	0.0001
β_3 (cat. conc.)	+183.66	0.0003
β_{11} (time)	+0.05293	0.6598
β_{22} (molar ratio)	-1.9870	0.0001
β_{33} (cat. conc.)	-62.906	0.0001
β_{12} (time and molar ratio)	+0.49167	0.0628
β_{13} (time and cat. conc.)	-0.59444	0.6821
β_{23} (molar ratio and cat. conc.)	-4.4417	0.0001

4. Results and Discussion

4.1. Effect of catalyst content

It was observed that the ester yield decreased with the increase in sodium hydroxide concentration. With 1.2% catalyst concentration, a complete soap formation was observed. This is because the higher amount of catalyst caused soap formation (see Figure 2).

4.2. Fatty acid content analysis

Fatty acid contents are the major indicators of the properties of bio-diesel since the amount and type of fatty acid content in the bio-diesel largely determine its viscosity. Bio-diesel from the waste cooking oil contained the highest amount of FFA content (calculated as oleic acid), an average 4.4%. The pure vegetable oils contained only about 0.15%, which are within permitted levels for being used directly for reaction with an alkaline catalyst to produce bio-diesel [7].

4.3. Properties of diesel fuel and biodiesel analysis

The fuel properties of diesel fuel and bio-diesel are presented in Table 4. The calorific values of the bio-diesel were found using a "bomb calorimeter" to be about 37 MJ/kg. However, the calorific value of standard diesel fuel was 42.5 MJ/kg, about 13% more than the bio-diesel. The reason for the lower value is because of the presence of chemically bound oxygen in vegetable oils which lowers their calorific values. It is also shown in Table 4 that the kinematic viscosity of vegetable oil was found to change from 33.72 to 4.53

mm²/s at 40 °C, this is a significant change. The initial high viscosity of that oil is due to its large molecular mass in the range of 600-900, which is about 20 times higher than that of diesel fuel, Barnwal et al [6].

4.4. Response surface methodology analysis

Table 3 lists the regression coefficients and the corresponding *p*-values for the second-order polynomial model. It can be that the regression coefficients of the linear terms for methanol/oil molar ratio and catalyst concentration (*M* and *C*, respectively), the quadratic terms in *M*² and *C*², and the interaction terms in *TC* and *TM* had significant effects on the yield (*p*-value <0.05). Among these, *M*, *C*, *C*² and *MC* were significant at the significance level, while *M*² and *TM* were significant at the level. Using the coefficients determined from Design-Expert 8.0 software program, the predicted model in terms of uncoded factors for methyl ester yield is:

$$y = -121.52 - 1.29T + 32.05M + 183.66C + 0.49TM - 0.59TC - 4.44MC - 0.05T^2 - 1.99M^2 - 62.91C^2$$

The results presented in Table 3 suggest that linear effects of changes in molar ratio (*M*) and catalyst concentration (*C*) and the quadratic effect *C*² were primary determining factors on the methyl ester yield as these had the largest coefficients. That the quadratic effect, *M*² and the interaction effect *MC* were secondary determining factors and that other terms of the model showed no significant effect on *y*. Positive coefficients, as with *M* and *C*, enhance the yield. However, all the other terms had negative coefficients. The response surface profile and its contour of the optimal production of yield based on equation above are shown in Figures 3, 4 and 5.

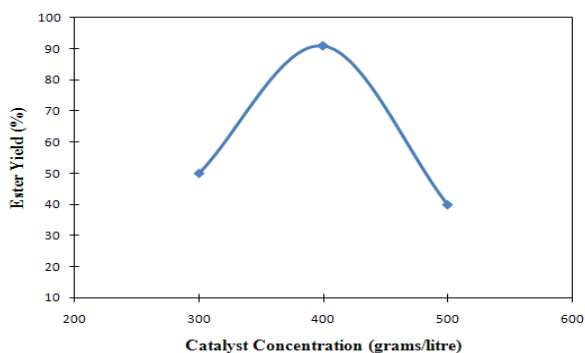


Fig. 2: Effect of catalyst on ester yield conversion.

Table 4: Properties of biodiesel in comparison with the ASTM standard of diesel and biodiesel.

#	Experimental results			ASTM D975	ASTM D6751
	Vegetable oil	Bio-diesel	Diesel	Diesel	Bio-diesel
Density(kg/m ³) at 15°C	920	885	845	-	-
Kin. Viscosity (mm ²) at 40°C	33.72	4.53	2.4	1.9-4.1	1.9-6.0
Calorific value (MJ/kg)	37.26	37	42.54	-	-
Cloud point (°C)	7.2	1	-5	-15 to 5	-3 to 12
Pour point (°C)	-15	-6	-17	-35 to -15	-15 to 16
Flash point (°C)	274	173	76	60-80	100-170
Cetane number (ignition quality)	NA	60	50	40-55	48-60
Iodine number	96.8	NA	NA	-	-

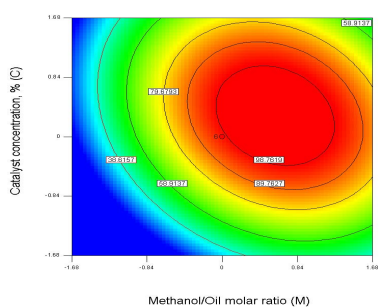


Fig. 3: Effect of M/O molar ratio and catalyst on methyl ester production.

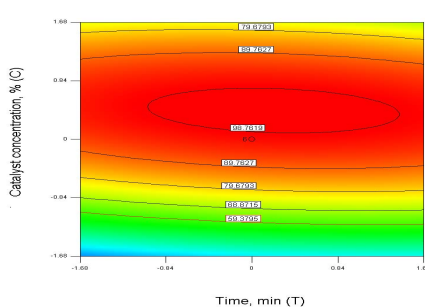


Fig. 4: Effect of reaction time and catalyst on methyl ester production.

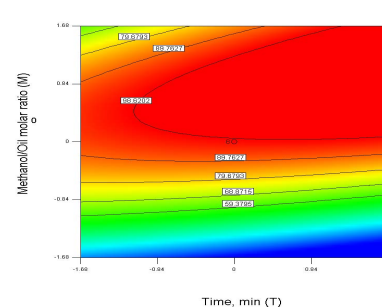


Fig. 5: Effect of M/O molar ratio and reaction time on methyl ester production.

4.5. Engine exhaust emissions analysis

The variation of THC, CO, CO₂ and NO_x emissions at different loads for standard diesel and six biodiesels at 1500 rpm are shown in Figures 6, 7, 8 and 9. From the figures below, it can be seen that all the biodiesels produced relatively lower THC, CO, and CO₂ emissions compared to standard diesel. This may be attributed to the availability of oxygen and high cetane number in biodiesel, which facilitates better combustion. On average over the four loads used in the tests, there was a reduction of 33.9% in hydrocarbon emission for WVO biodiesel, whereas it was 25.9% and 26.4% for sunflower oil biodiesel and rapeseed oil

biodiesel respectively. In addition, at full load CO₂ emissions from biodiesel operations were, on average, 22% lower than those of standard diesel operation. On the other hand, in bio-diesel operation, there was an average of 12.5% increase in the NO_x emission was measured compared to standard diesel operation. The oxygen content of bio-diesel is the main reason for higher NO_x emissions because the oxygen in the biodiesel can react easily with nitrogen during the of combustion process, thus causing higher emissions of NO_x.

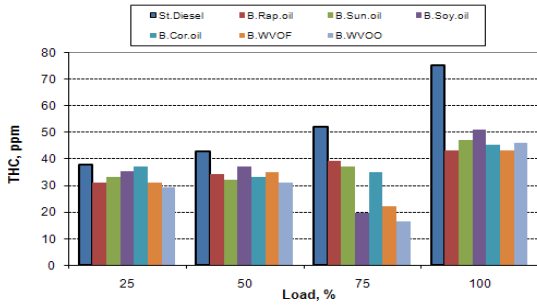


Fig. 6: Hydrocarbon against engine load at 1500 rpm.

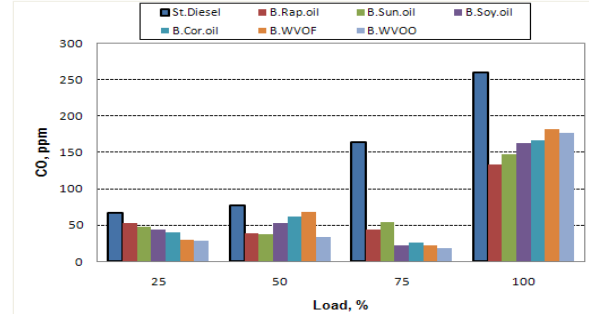


Fig. 7: Carbon monoxide against engine load at 1500 rpm.

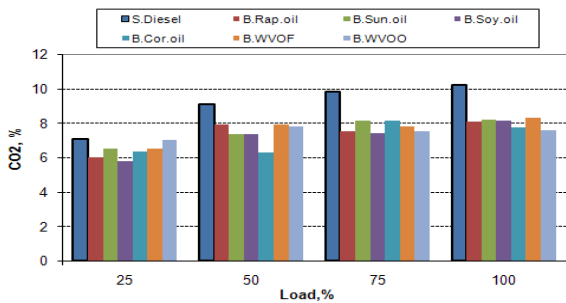


Fig. 8: Carbon dioxide against engine load at 1500 rpm.

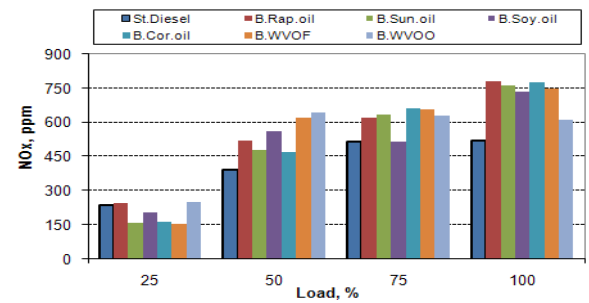


Fig. 9: Oxides of nitrogen against engine load at 1500 rpm.

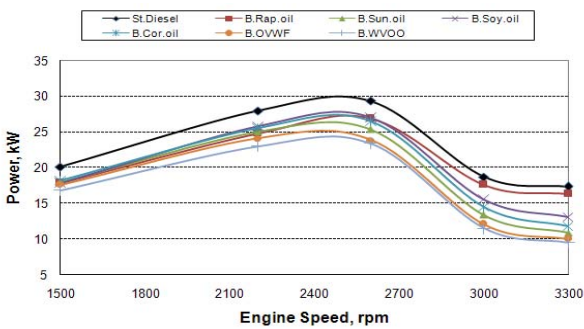


Fig. 10: Average power output against engine speed at full load with standard diesel and biodiesels as fuel.

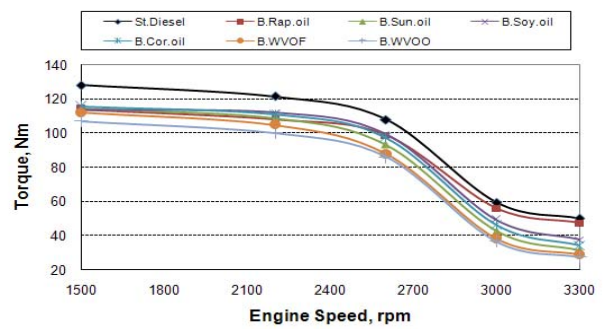


Fig. 11: Average torque output against engine speed at full load with standard diesel and biodiesels as fuel.

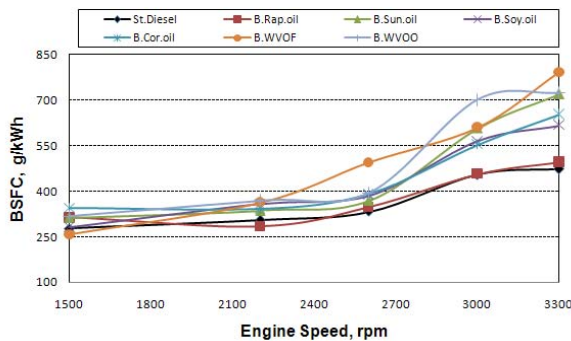


Fig. 12: Average BSFC with engine speed at full load with standard diesel and biodiesels as fuel.

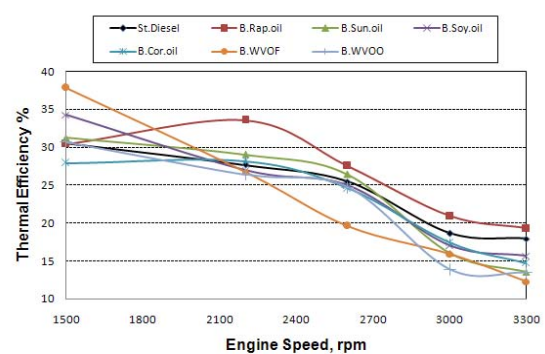


Fig. 13: Average brake thermal efficiency against engine speed at full load with standard diesel and biodiesels as fuel.

4.6. Engine performance analysis

Figures 10, 11, 12 and 13 show the variation in the brake power, brake torque, brake specific consumption (BSFC) and thermal efficiency with the engine speed of the test engine operated at full load with standard diesel and bio-diesel. The brake power of the engine with standard diesel was higher than for any biodiesel. Because the biodiesels have lower calorific values than that of standard diesel, both torque and brake power is reduced. However, difference in brake power and brake torque between standard diesel and the biodiesels were very small in most cases. The BSFC is the ratio of the fuel consumed in g/sec to the engine brake power. The BSFC for biodiesel operation was on an average 11.6% higher than that for standard diesel operation. This increase may be attributed to the collective outcomes of the higher fuel density, higher fuel consumption and lower brake power due to lower calorific value of the biodiesel. In addition, it was seen that biodiesel has higher thermal efficiency than standard diesel. The improvement of thermal efficiency with biodiesel can be attributed to the oxygen content and higher cetane number of bio-diesel.

5. Conclusions

The “Fulpod” processor was used for the production of biodiesel from vegetable oils by using the alkali-catalyzed transesterification process. The fuel properties, such as kinematic viscosity, density, calorific value and cloud, pour and flash point, were measured. After esterification of vegetable oils, the kinematic viscosity was reduced from 40 mm²/s to 5 mm²/s. From the literature review it was apparent that by running a biodiesel there would be a decrease in emissions present while a slight decrease in engine efficiency. The experiential data did confirm these claims showing decreases in almost all the emissions (CO, THC and CO₂) except for NO_x. RSM proved to be a powerful tool for the optimization of methyl ester production at a fixed temperature. A second-order model was successfully developed to describe the relationships between methyl ester yield and test variables, including methanol/oil molar ratio, catalyst concentration, reaction temperature, rate of mixing and reaction time. The optimal conditions for the maximum methyl ester yield were found to be at methanol/oil molar ratio of 6:1, NaOH catalyst concentration of 1% (by the weight of vegetable oil), reaction temperature 65°C, rate of mixing 300 rpm and a reaction time of 70 min. This optimized condition was validated with actual bio-diesel yield in 97.5%.

6. References

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