Research Article

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Experimental Investigation of Adding Antioxidants into the Algae Biodiesel Blend as a Diesel Engine Fuel

N. Krishnamoorthy[1*], K. Vinothkumar[2], S. Dhivakar[1] and K. Anbumani[1]

[1]Department of Mechanical Engineering, P.T.Lee Chengalvaraya Naicker College of Engineering and Technology, Oovery, Kanchipuram, TN, India

[2]Department of Mechanical Engineering, SRM Institute of Science and Technology, Ramapuram, Chennai, TN, India

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*krishme86@gmail.com

ABSTRACT

This study investigates the use of a blended fuel composed of 20% microalgae-based biodiesel and 80% conventional diesel (by volume) as a sustainable alternative for compression ignition (CI) engines. While this biodiesel-diesel blend offers environmental benefits, it results in slightly increased emissions of nitrogen oxides (NO_x) compared to pure diesel. To address this issue, antioxidants were incorporated into the fuel blend to reduce NO_x emissions and enhance storage stability. Pure biodiesel is prone to thickening in cold climates and can promote oxidative degradation of metal storage tanks; the addition of antioxidants helps mitigate these challenges by improving oxidative resistance.Experimental evaluations were conducted using standardized testing procedures defined by the American Society for Testing and Materials (ASTM) under varying engine loads. Performance and emission characteristics—specifically carbon monoxide (CO), nitrogen oxides (NO_x), and brake thermal efficiency (BTE)—were analyzed. Results showed significant emission and performance improvements: NO_x emissions were reduced by 1070 parts per million (ppm) at a retarded injection timing of 20 degrees before top dead center (BTDC) using 250 ppm of butylated hydroxytoluene (BHT) and 500 ppm of pyrogallol (PY). CO emissions decreased by 0.02% at a normal injection timing of 20° BTDC without antioxidants. Additionally, a 35% increase in BTE was observed at normal injection timing of 23° BTDC with 500 ppm of antioxidants, under full-load conditions with the B20 blend. These findings highlight the combined effectiveness of antioxidant additives and optimized injection timing in enhancing both engine performance and emission control.

Keywords: Emission; Diesel engine; Antioxidant; Algae biodiesel; Injectable timing.

1.INTRODUCTION

Studies on alternative energy sources are getting more and more important every day due to the growing energy demand and pollution (Ibrahim and Ali, 2017). A number of environmental problems emerge due to the use of fossil fuels in IC engines (Edwin *et al.* 2017). Developing nations have found a solution by converting vegetable oils into biodiesel using catalysts (Ambarish, and Bijan, 2017a). Researchers choose biodiesel based on its sustainable, cost-effective and environmentally beneficial characteristics (Ambarish and Bijan, 2017b) Analyzing the advantages of using a cheap oil that is not edible can assist in reducing the cost of biodiesel production, which is required for producing biodiesel on a commercial scale (Lai *et al*. 2015). Several researchers have systematically worked on using vegetable oils along with conventional fuels in engines. Consequently, there will be less demand for fossil fuels. Since plant-based oils are renewable and do not emit harmful gases, these have the potential to replace fossil fuels, at least partially (Basavaraj *et al.* 2016). These vegetable oils suffer fromhigh viscosity, low heat capacity, gum formation and auto-oxidation, and affect engine life.

Using these oils without any direct engine adjustment may result in engine damage and poor performance. Direct use of vegetable oils on the piston rings may lead to contamination. Therefore, some preliminary steps are required to convert vegetable oils into well-functioning fuels. Vegetable oils can be made useful by various techniques. Algal oils are obtained through the solvent removal process using n-hexane. Blending vegetable oils with diesel has resulted in reduced nitrogen oxides and other smokes (Satputaley *et al.* 2018).

A promising alternative with significant reductions in CO_2 and NO_x is the use of emulsions instead of blends or pure biodiesel (Ramón*et al.*2017). Asokan *et al.* (2019) have investigated the performance of different biodiesel-diesel blend sand found higher performance characteristics by blended fuel in comparison with pure fuel.

Mofijur*et al*. (2019) used waste cooking oil to increase engine efficiency and reduce exhaust gas emissions in order to reduce the quantity of pollutants emitted into the environment. Saravanan and Krishnamoorthy, (2020) and Saravanan *et al*. (2021) focused on the factors, injection timing and addition of

antioxidants to investigate the engine performance with different biodiesel blends.

Krishnamoorthy *et al*. (2024) used nanocrystalline copper oxide additive to improve engine performance and reduce hazardous emissions. In a compression ignition engine, this study optimized algal oil-diesel mixes with antioxidants (butylated hydroxytoluene and pyrogallol). Krishnamoorthy *et al*. (2025) used the Taguchi-Grey approach in conjunction with the analytical hierarchy process to improve brake thermal efficiency and minimize NO_x emissions. Amala and Arunraj (2024) have reported that algae biodiesel enhanced with nano-additives exhibited substantial improvements in brake thermal efficiency and a marked reduction in NO_x and CO emissions, reinforcing the potential of antioxidant-enriched algal biodiesel blends for cleaner CI engine operation.

The primary objective of this study is to investigate the type, ratio and mechanism of antioxidants influencing engine performance and emissions as a function of injection timing.

2. MATERIALS AND METHODS

Spirulina maxima was harvested from a pond in Chennai, Tamil Nadu, India. Crude algal oil was obtained from dry biomass using a Soxhlet apparatus. Chemicals such as methanol (99.8%), ethanol (99%), potassium hydroxide (KOH) (99.6%), phenophtaline, hydrochloric acid (99%), sulfuric acid (96%), and distilled water were procured from the local suppliers in Chennai.

2.1 Pre-treatment of Algae Biomass

Spirulina maxima algae was thoroughly cleansed in fresh water, dried in shade, and heated in an oven at 70°C to remove moisture. Then, a mechanical crusher was used to turn the dry biomass into a fine-grained powder as shown in Fig.1. This was then blended in a 1:3 (v/v) ratio with water by ultrasonication using a 24 kHz frequency and a 50°C temperature maintained for 5 minutes.



Fig. 1: Spirulina maxima algae powder

2.2 Extraction of *Spirulina maxima* Algal Oil

The oil was extracted from the pre-treated algal biomass sample using a Soxhlet device. In this procedure, the pre-treated *Spirulina maxima* biomass was fed to the Soxhlet apparatus as shown in Fig. 2. Oil was extracted by percolating algal biomass for 48 hours at 45°C in a solution of n-hexane and 15% diethyl ether (DEE) and 10% dichloromethane`. Due to its non-polar phenomena, DEE is used as an extraction solvent. Dichloromethaneaids separation of water from oil.

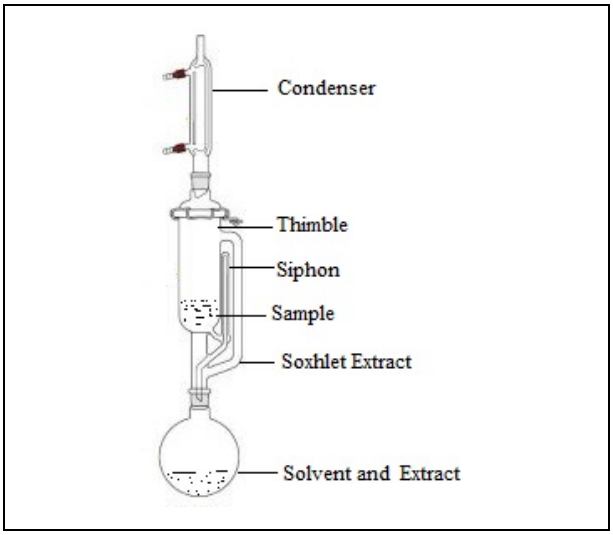


Fig. 2: Soxhlet apparatus

2.3 Esterification Process

The esterification process is an essential pretreatment step in the production of biodiesel from microalgae oil, particularly when the oil contains a high percentage of free fatty acids (FFAs). Microalgal oil often exhibits elevated FFA levels, which can interfere with the subsequent transesterification process by promoting soap formation when base catalysts are used. To address this, esterification is employed to convert FFAs into fatty acid esters using an alcohol—commonly methanol—in the presence of an acid catalyst such as sulfuric acid (H_2SO_4). During this reaction, FFAs react with methanol to form methyl esters (a type of biodiesel) and water. The process is typically carried out under controlled conditions, with a methanol-to-oil molar ratio of 6:1 to 12:1, a catalyst concentration of 0.5% to 1% by weight of oil, temperatures between 50°C and 60°C, and a reaction time of 1 to 2 hours. Once the reaction is complete, the mixture is allowed to settle, enabling the separation of the ester-rich phase from water and impurities. This pretreatment step significantly reduces the FFA content, making the algal oil suitable for efficient transesterification, and ultimately improving biodiesel yield and quality.

2.4 Transesterification Process

After being heated to 55°C, the algae oil was added to the glass reactor. The catalyst KOH of 0.75 wt.% was dissolved in methanol at a methanol-algae oil molar ratio of 9:1 in a separate flask. The mixture was allowed to react for one hour with a constant stirring speed of 600 rpm using a mechanical stirrer and allowed to stand for two hours in a different reactor to separate the glycerol and biodiesel layer.

2.5 Preparation of Fuels

Fig. 3 shows the prepared samples and Table 1 shows the properties of diesel and algae biodiesel. Biodiesel and diesel fuel have very similar density and viscosity. Antioxidant additives were added to the B20 biodiesel blend (20% biodiesel + 80% diesel). Biodiesel is mixed with two antioxidant additives in three different concentrations: 0 ppm, 250 ppm, and 500 ppm butylated hydroxytoluene (BHT) and pyrogallol (PY). The engine was run under three distinct load conditions, and the diesel only test outcomes were compared.

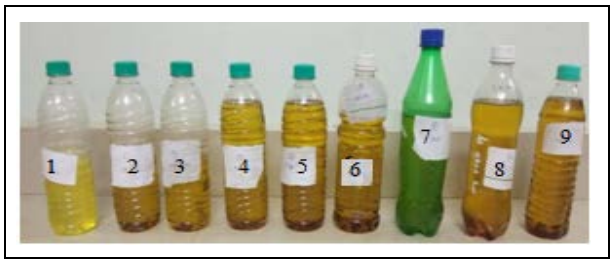


Fig. 3: Prepared samples

Table 1. Properties of diesel and algae biodiesel

Properties	Diesel (B00)	Algae Biodiesel (B20)
Density(kg/m^3) at 15°C	830	836.5
Viscosity(mm^2/s) at 40°C	2.9	3.26
Cetane number	45-55	48.88
Calorific Value (MJ/kg)	42.5	42.2
Flash point (°C)	76	86.4
C (%)	87	84.9
H (%)	12.6	12.51
O (%)	0.4	2.48

2.6 Engine Set-up

The engine layout used in this study is a single-cylinder, air-conditioned, vertical, direct injection CI engine. When connected to an eddy current dynamometer, it can produce 4.4 kW and run continuously at 1500 rpm. The air heater, air temperature sensor and anti-pulsating drum are on the fuel intake side ofthe engine. The EGT indication, smoke instrument, and exhaust gas tester are on the exhaust side of the engine. The setup also includes a separate fuel computing device to track the amount of algae biodiesel mixture consumed. The test apparatus also comes with 64-bit DAQ system to collect data on cylinder pressure and crank angle.

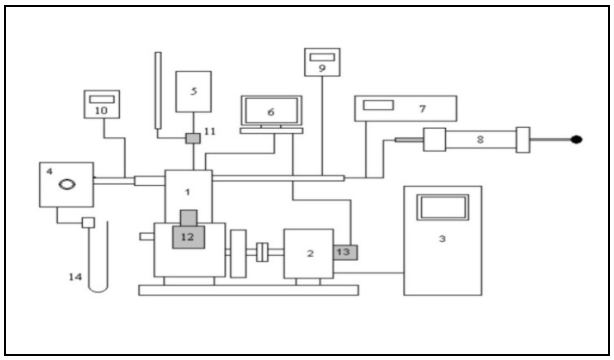


Fig. 4: Engine layout (1) Diesel generator, (2) Dynamometer with eddy current, (3) Dynamometer management, (4) Drum that resists throbbing, (5) TD mixes, (6) P-IV DAV-equipped computer, (7) Gas fumigator analyzer, (8) Pump for sampling smoke, (9) Indicator of exhaust temperature, (10) Indicator of air intake temperature, (11) Two-way valve, (12) Pump for fuel injection, (13) Angle encoder for crank, and (14) Manometer

Fig. 4 displays the structural diagram of the experimental setup. Table 2 lists the technical details of the engine utilized in the current study. An electrical dynamometer with a swinging sphere was employed to put the engine under load. A solid frame for moving space type loading and a 5-KVA generator for AC power (220V, 1500 rpm) are attached to this electrical dynamometer. A strain instrument-style load chamber was used to accurately measure the response torque to determine output power. To dissipate the power produced, a water rheostat was incorporated with a variable depth of the dipping electrode. The advancement of the thickness of the shim was changed to alter the timing of injection time.

Table 2. Engine specification

Kirloskar Model, TAF1 Make	
Bore	87mm
Stroke	110mm
Compression ratio	17.5:1
Swept volume	660 cm^3
Power rating	4.5 KW
Speed rate	1500 rpm
Timing of injection	23° CA Btdc
Injection pressure	210 bar
Type of injection	Direct Injection
Diameter of orifice Discharge	13.5 mm
Coefficient	0.61

Table 3. Test conditions of the engine

Ex. No.	Timing of Fuel Injection	Fuel
1.	Normal Timing (23 BTDC)	Diesel
2.	Normal Timing (23 BTDC)	B20
3.	Normal Timing (23 BTDC)	B20 along with PY and BHT
4.	Timing of Retarded Injection (20 BTDC)	B20 along with PY and BHT
5.	Timing of Advanced Injection (26 BTDC)	B20 along with PY and BHT

2.7 Adjustment of Injectable Timing

Engine emissions significantly change if the normal injectable timing for fuel injection is changed. Additionally, the advance and retard angles were limited to three crank angle degrees (CAD) to prevent negative effects (increased other emissions). Shims positioned below the flange of fuel injection pump could be added or removed to change the static injection timing. Shims with 0.3 mm thicknesses were used in the current study. Depending on whether a shim is added to the pump or removed, each shim can advance or retard the crank angle by 3°. The combinations of timing of injection and fuel chosen for this study are shown in Table 3. Table 5 shows the matrix of experimental trail.

Table 4. L9 Orthogonal array (OA)

Exp. No.	Factor 1	Factor 2	Factor 3
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

To build the Experimental test matrix, the Taguchi Orthoganaol array (OA) methodology was used. It was concluded that L9 is the optimal OA for more than two of the three level criteria. The table 5 Experimental test matrix has been designed similar to the L_9 Orthogonal Array (OA) table 4.

2.8 Engine Testing

Engine tests were conducted using diesel and B20 fuel under various engine loading conditions. A variety of responses were noted, including fuel consumption and emission parameters. The experiments were conducted using the structure listed in Table 5. Engine emission parameters were measured with an AVL smoke meter and an exhaust gas meter.

Table 5. Experimental test matrix

Exp. No.	Timing of Injection (CAD)	PY (ppm)	BHT (ppm)
1.	23	0	0
2.	23	250	250
3.	23	500	500
4.	26	0	250
5.	26	250	500
6.	26	500	0
7.	20	0	500
8.	20	250	0
9.	20	500	250

3. RESULTS AND DISCUSSION

3.1 Performance Characteristics

3.1.1 Brake Thermal Efficiency

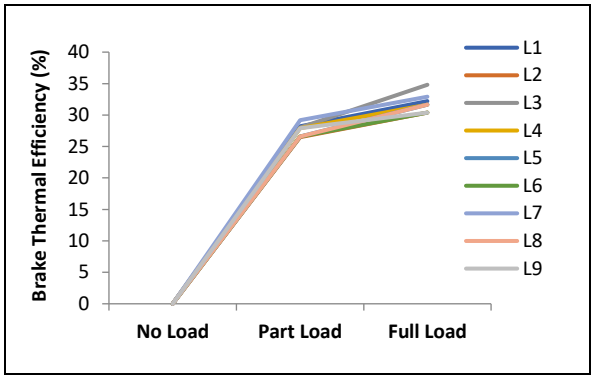


Fig. 5: BTE variation in relation to load in various combinations

When compared to other combinations, combination 3 with injectable timing set at 26° BTDC has the highest and most stable brake thermal efficiency under almost all operating conditions (Fig. 5). Therefore, this combination is most effective. Fuel injection retardation had insufficient time for air-fuel mixing and poor combustion was noted. On the other hand, advancing the fuel injection timing at 26° BTDC resulted in improved combustion process and hence higher BTE was observed. This was due to enough residence time for air-fuel mixture preparation in the cylinder with longer combustion duration. Brake thermal efficiency reaches its maximum with better combustion at higher oxygen content and advanced injection.

Fig. 6 shows that injectable timing has the largest impact on BTE, followed by antioxidant

additives. At 100% load conditions, the percentage contribution of injection time reaches its maximum at around 80%. This is so that the combustion rate can be controlled by the injectable timing. This shows that brake thermal efficiency increases with increasing load.

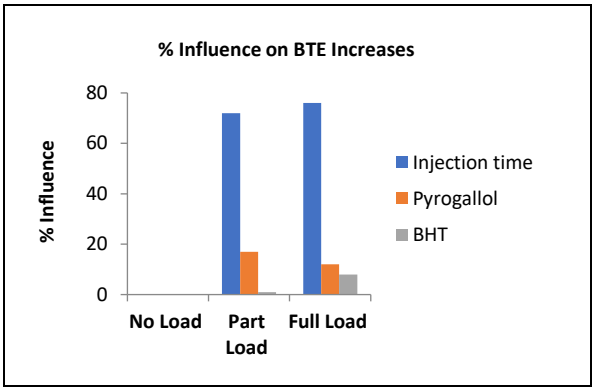


Fig. 6: Percentage influence of each factor on BTE

3.2 Emission Character of the Engine

3.2.1 Oxides of Nitrogen Emission (NO_x)

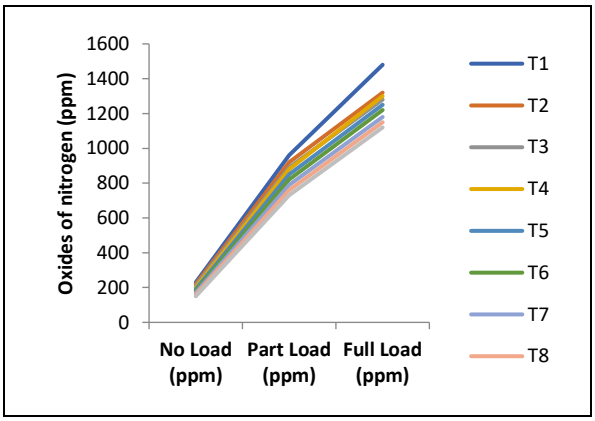


Fig. 7: NO_x variation in relation to various combinations of load

Fig. 7 shows that, compared to other combinations, combination 9 produces the lowest amount of NO_x as load increases. It is noted that when injectable timing is advanced, NO_x emissions from diesel and algae biodiesel engines increase considerably under the suggested load and speed conditions. This is because additional mixture of fuel-air is burnt throughout the premixed combustion stage due to the increased delay and higher temperatures that are generated. However, both fuels produced lower NO_x emissions when the injectable timing was delayed. As a result, the fuel-air mixture burns for a shorter time when injectable timing is delayed and thus reduces high temperatures and NO_x.

Injectable timing has a large impact on reducing NO_x (Fig. 8). This is due to the fact that by postponing the injection and allowing the temperature to rise slowly, the production of free radicals at high temperatures is reduced. In contrast, the inclusion of additives has a relatively small impact. Antioxidants restrict the production of peroxyl radicals that are free through their reaction with aromatic amines. The main reason why biodiesel releases more NO_x is because of these peroxyl free radical formations. The rate of oxidation reaction is controlled by free radicals, which are unpaired electrons in molecules.

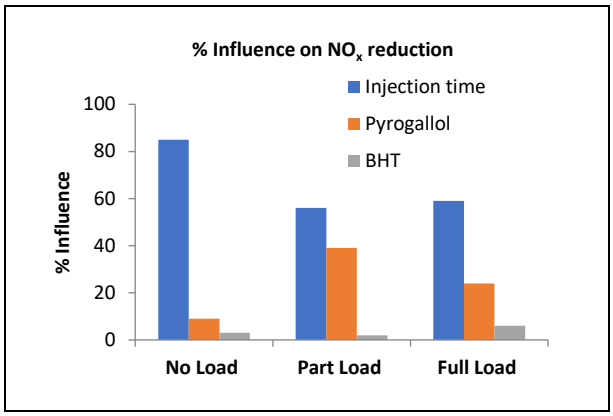


Fig. 8: Percentage influence of each factor on NOx reduction

3.2.2 CO Emission

Fig. 9 shows that the first combination has the lowest CO emissions as there are no antioxidants and no injection time delay. When antioxidants are added complete combustion does not occur, resulting in high concentrations of CO. The relationship between NO_x and CO emissions is inversely proportional as low NO_x indicates incomplete combustion, which increases CO.

The amount of fuel burnt is controlled by the timing of injection. Advanced injection reduces CO levels while retarded injection increases CO. Antioxidants reduce the amount of oxidants that can be used to produce CO from unburnt carbon molecules, which reduces CO (Fig. 10).

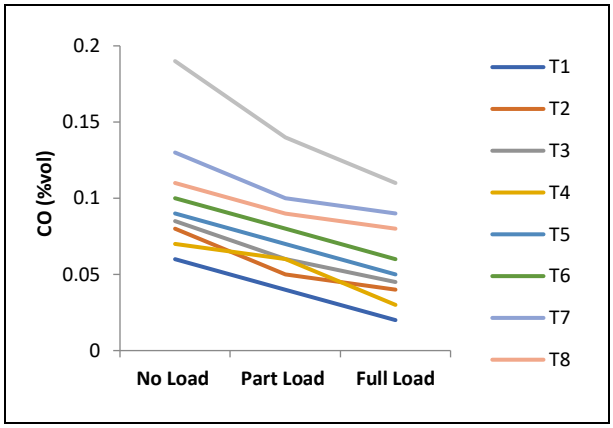


Fig. 9: CO variation in relation to load in various combinations

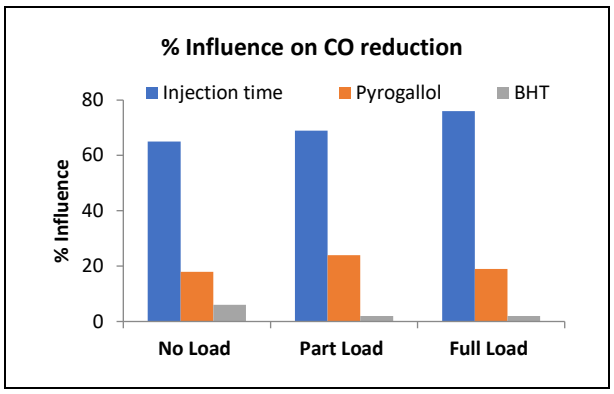


Fig. 10: Percentage influence of each factor on CO reduction

4.CONCLUSION

This study evaluated the combined effects of antioxidant additives and injection timing on the control of nitrogen oxides (NO_x) emissions from a diesel engine fueled with microalgae-based biodiesel, with attention to minimizing adverse impacts on carbon monoxide (CO) emissions and brake thermal efficiency (BTE). Two antioxidants, pyrogallol and butylated hydroxytoluene (BHT), were tested in various concentrations under different injection timings. The results indicate that injection timing had the most significant influence on all measured parameters. At full load, advancing or retarding injection timing led to a substantial improvement in BTE, with a maximum increase of approximately 76%, and contributed to a 59% reduction in NO_x emissions. Similarly, CO emissions were most effectively reduced by injection timing adjustments, achieving up to 77% reduction. Among the parameters studied, injection timing at 26° before top dead center (BTDC) had the greatest overall impact. Pyrogallol at a concentration of 500 ppm emerged as the second most effective factor in reducing NO_x, while BHT at 250 ppm had the least influence. These findings confirm that a strategic combination of optimized injection timing and antioxidant supplementation can significantly enhance engine performance while reducing harmful emissions when using algae-based biodiesel.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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