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Effect of Blending on Cold Flow Properties of Biodiesel Produced from Waste Frying Oil

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Abstract: Recycling waste frying oils is a significant environmental and economic issue. Biodiesel production from waste frying oil is an effective method to obtain a sustainable energy source. Waste frying oil is considered an essential source of biodiesel production. Biodiesel fuel made from fats or oils, such as waste frying oil with high levels of saturated fatty compounds, tends to have high cold flow properties (CFPs). Waste frying oil (WFO) was sourced from a cafeteria on Near East University's campus and underwent a transesterification reaction to produce biodiesel fuel. The cold flow properties of WFO based-biodiesel—CP (cloud point), PP (pour point), and CFPP (cold filter plugging point)—were measured at 15°C, 11°C, and 13°C, respectively, following current ASTM and EN standards. These temperatures were also assessed for blends of biodiesel and commercial diesel. Due to its cold flow characteristics, pure biodiesel can be effectively utilized from May to October in Lefkoşa. However, appropriate blends of biodiesel and commercial diesel can be formulated for use during the winter season.

Keywords: Biodiesel, Waste frying oil, Cold flow properties

Introduction

The rise in population and higher food consumption rates has led to a surge in waste frying oil (WFO) from various sources such as households, restaurants, hotels, schools, and industries. Due to its island status, Cyprus faces a particularly severe situation compared to mainland areas. Improper disposal of WFO through sinks and drains poses significant challenges for sewage treatment facilities, consequently driving up purification expenses. Indeed, WFO represents a valuable residue that holds potential as a raw material for various purposes such as soap manufacturing, energy generation through anaerobic digestion, thermal cracking, and biodiesel fuel production (Phan & Phan, 2008; Sabudak & Yıldız, 2010; Al-Shanableh et al., 2023).

Biodiesel stands out as a popular alternative in liquid fuels, primarily due to its compatibility with conventional diesel engines with minimal or no adjustments required and its ability to be blended with petroleum diesel. Since the 1970s, various methods have been used to produce low-viscosity biodiesel from vegetable oil, such as pyrolysis, micro-emulsification, or transesterification. Transesterification, a reaction catalyzed by a base, acid, or enzyme, involves reacting virgin vegetable oil, waste frying oil (WFO), or animal fat with an alcohol to produce fatty acid methyl esters (FAME), or biodiesel, along with glycerol as a co-product, which has commercial value. Base-catalyzed transesterification is considered the most promising method for reducing viscosity. In this process, triglycerides react with methanol, releasing three fatty acid chains from the glycerol skeleton, which then combine with alcohol to form fatty acid methyl esters and glycerol (Encinar et al., 2007; Al-Shanableh, 2017). The primary biodiesel standards that serve as benchmarks for others are EN 14213 (Heating Fuels) and EN 14214 (Automotive Fuels), along with ASTM D6751-09. It is well-recognized that diesel fuel tends to gel or solidify at low temperatures. Biodiesel, however, tends to gel at higher temperatures than diesel fuel and exhibits poor cold flow properties (CFPs) (Evcil et.al., 2018). There are three critical parameters for assessing the CFPs of biodiesel: cloud point (CP), pour point (PP), and cold filter plugging point (CFPP). The CP is the temperature at which the first visible cloud of wax crystals forms when the fuel is cooled under specified conditions as described by ASTM D2500-09 or ISO 3015:1992. The PP is the temperature at which enough wax crystallizes to gel the fuel, rendering it unable to flow. The sample must be cooled according to the procedures outlined in ASTM D97-05 or ISO 3016:1994. The CFPP, described in ASTM D6371-05 and EN 116:1998, directly impacts the performance of diesel engines in winter. It signifies the lowest temperature at which 20 ml of fuel can pass through a 45-micron screen in 60 seconds under a 200 mm water (1.96 kPa) vacuum. The CP represents the highest temperature for assessing cold flow, while the PP is the lowest. The CFPP typically falls between the cloud and pour points. While the ASTM D6751 standard requires the CP, the EN 14213 and EN 14214 standards specify the PP and CFPP instead of the CP.

CFPs of WFO-based biodiesels are poorer compared to virgin vegetable oil-based biodiesel. One method to ameliorate this problem would be to blend biodiesel produced from WFO with petroleum-based diesel fuel or biodiesel produced from crude vegetable oils (Al-Shanableh et al., 2023). Bhale et al. (2009) examined how ethanol, kerosene, and commercial fuel blending impact the cold flow characteristics of biodiesel and found a considerable reduction in PP. Dwivedi and Sharma (2016) also added ethanol with different fractions to WFO-based biodiesel, showing improved CFP of blended biodiesel.

In this study, two types of raw materials, WFO rich in saturated fatty acids and refined canola oil (RCO) abundant in unsaturated fatty acids, underwent a single-step base-catalyzed transesterification process to produce biodiesel fuel called waste frying oil methyl ester (WFOME) and refined canola oil methyl ester (RCOME), respectively. Subsequently, the CFPs produced by the WFOME and RCOME, including CP, PP, and CFPP, were measured according to ASTM and EN standards. Three methods were employed to explore the effect of blending on the reduction of cold flow temperatures of WFOME. In the first method, WFO and RCO were mixed in varying ratios before undergoing transesterification, while in the second method, RCOME and WFOME were blended in different volume ratios. Furthermore, the third and the last, WFOME, was blended with commercial diesel fuel in different volume ratios. Resultant CFPs were measured and compared.

Materials and Methods

Materials

WFO was sourced from the cafeterias of Near East University, where approximately 18 to 20 liters of WFO were gathered daily per cafeteria and RCO was purchased from a local supermarket. Anhydrous methanol (MeOH) with a purity of 99.8% and high-purity sodium hydroxide (NaOH) were procured from Merck for the experiments. The feedstocks' fatty acid (FA) compositions were analyzed using the EN ISO 5508 method at the TRNC Ministry of Health, Directorate State Laboratory in Nicosia, utilizing Gas Chromatography (GC). The findings from the GC analysis are presented in Table 1.

Table 1. Fatty acid compositions of WFO and RCO

Fatty acid	**Molecular mass (g/mol)**	**% Fatty acid of WFO**	**% Fatty acid of RCO**
Caprylic acid - C8:0	144.21	0.05	0.0
Capric acid - C10:0	172.27	0.33	0.0
Lauric acid - C12:0	200.32	1.18	0.08
Myristic acid - C14:0	228.38	0.10	0.0
Palmitic acid - C16:0	256.43	39.29	5.63
Palmitoleic acid – C16:1	254.41	0.14	0.0
Stearic acid - C18:0	284.48	4.04	1.57
Oleic acid - C18:1	282.47	40.42	62.97
Linoleic acid - C18:2	280.45	13.84	21.34
Linolenic acid - C18:3	278.44	0.18	6.99
Arachidic acid - C20:0	312.54	0.0	0.46
Eicosenoic acid - C20:1	310.5	0.0	1.04

Experimental Set-up for Base-Catalyzed Transesterification

Figure 1 outlines the sequence of experimental steps that were employed to produce biodiesel through a base-catalyzed one-step transesterification reaction. While transesterification constitutes the primary phase in biodiesel production, adhering to international standards requires additional procedures such as raw material pretreatment, separation of reaction products, and purification of the resultant products.

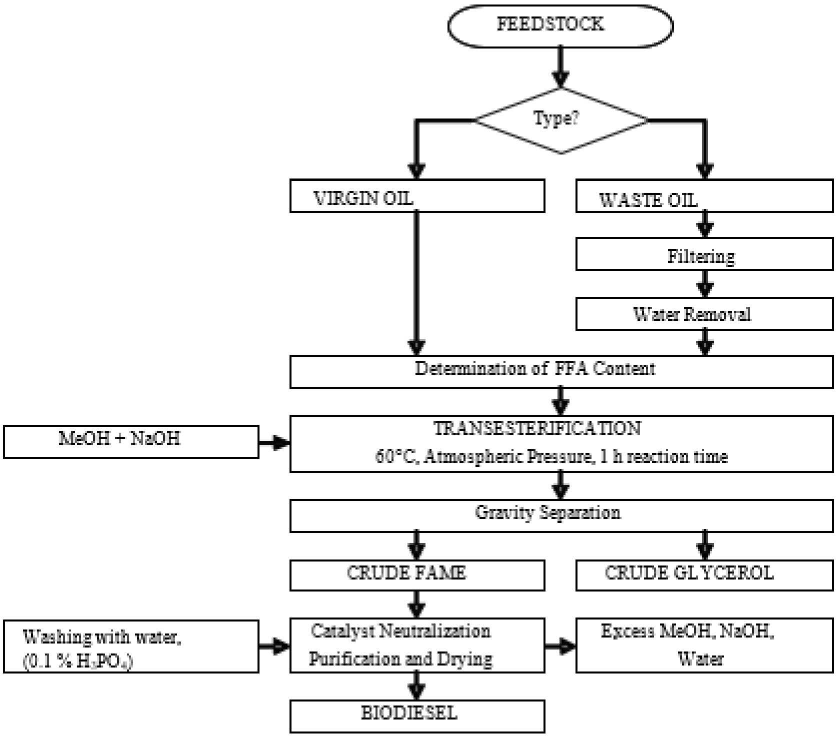

Figure 1. Flowchart of the experimental procedure for base-catalyzed transesterification

Determination of Some Physicochemical Characteristics and CFPs

Besides CFPs, some physicochemical properties of biodiesel produced were also determined to ensure the quality of products. The biodiesel samples' CP, PP, and CFPP were determined using ASTM standards, specifically ASTM D2500-09, ASTM D97-05, and ASTM D6371-05, respectively. The CP and PP measurements equipment adhered to ASTM standards, as illustrated in Figure 2. Three T-type thermocouples were utilized for temperature measurements. Thermocouples T1 and T2 were designated for measuring the temperature of the biodiesel sample. However, thermocouple T3 was explicitly employed to gauge the temperature of ethanol in the region adjacent to the jacket near the mid-section. Thermocouple T1 was positioned 3 mm beneath the sample's surface for PP measurement, while T2 was situated 3 mm above the bottom of the test jar to determine CP and CFPP. For CFPP measurements, the same setup was utilized, along with incorporating a vacuum system and a pipette featuring a filter unit.

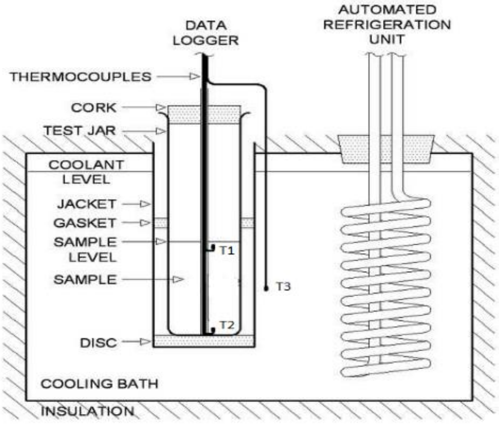

Figure 2. Experimental setup for CFP measurements

Blending Procedures

Three different methods were employed to explore the impact of blending on reducing the cold flow temperatures of WFOME. Method 1: WFO and RCO were combined in various proportions before undergoing transesterification. To target the reduction of CFP in WFOME, up to 50 vol % of RCO was blended with WFO. Blends were labeled according to composition, such as 100W0C, 90W10C, etc., for instance, in 100W0C, 100 vol % of WFO was mixed with 0 vol % of RCO. Method 2: Mixing RCOME and WFOME in different volume percentages. WFOME was blended with 0, 25, 50, 75, and 100 vol % of RCOME. Method 3: WFOME was blended with commercial diesel fuel on a volume basis. The commercial diesel fuel used was Euro diesel (EN 590:2009), obtained from a petrol station in Nicosia. Blends comprising 0, 5, 10, 20, 30, 40, 50, 70, 80, 90, and 100 vol % of commercial diesel were prepared.

Results and Discussion

Physicochemical Characteristics and CFPs of the Biodiesel Produced

WFOME and RCOME underwent fuel property assessments following either ASTM D6751 or EN 14214 standards. ASTM D6751 specifies the criteria that pure BD (B100) must meet before its use as a pure fuel or when blended with conventional diesel fuel. Conversely, EN 14214 outlines the minimal criteria for FAME (Fatty Acid Methyl Esters). Table 2 presents the fuel properties of the four BD samples tested and the thresholds outlined in the ASTM and EN standards.

Table 2. The fuel properties of WFOME and RCOME of the present study

	Method	**Limits**	**WFOME**	**RCOME**
Kinematic viscosity at 40 ˚C (mm^2/s)	ASTM D 445	1.9-6.0	4.666	4.582
Higher heating value (MJ/kg)	ASTM D 4809	35.0	40.14	39.23
Free glycerin (wt %, max.)	EN 14105	0.02	0.006	0.003
Total glycerin (wt %, max.)	EN 14105	0.25	0.248	0.196
Mono glyceride (wt %, max.)	EN 14105	0.80	0.62	0.64
Diglyceride (wt %, max.)	EN 14105	0.20	0.32	0.20
Triglyceride (wt %, max.)	EN 14105	0.20	0.34	0.1
Ester contents (wt %, max.)	EN 14103	96.5	96.5	97.0
Linoleic acid methyl esters (wt %, max.)	EN 14103	12.0	0.2	6.8
Iodine value (g I_2 / 100 g, max)	EN 14111	120	110	66
Cloud point (˚C)	D 2500		15	-3.5
Pour point (˚C)	D 97		12	-10
Cold filter plugging point (˚C)	D 6371		14	-7.5

The CFPs of biodiesel derived from WFO and RCO can be considered inferior compared to commercial diesel fuel No. 2, which boasts CP of -16°C, PP of -27°C, and CFPP of -18°C. Specifically, WFOME exhibits poorer CFP than RCOME. This discrepancy is primarily attributed to the substantial presence of saturated fatty acid compounds in waste frying oil samples and exceptionally high palmitic acid portions. Udomsap et al., 2008, observed that a high palmitic acid content (63 wt %) in palm stearin methyl ester led to a significant increase in CP and PP values, reported as 18°C and 19.4°C, respectively.

Based on data from the Meteorology Department of TRNC, the lowest average temperature recorded over the past ten years in January and February in Nicosia was approximately 2°C. All three CFP temperatures of BD produced from WFO exceeded 2°C. Consequently, pure WFOME may be suitable for use from May to October, covering six months of the year in Nicosia, while RCOME can be used year-round. A common approach to enhancing cold flow temperatures, including CFPP, involves blending commercial diesel fuel into the BD.

Effect of Blending in Improving the CFP of WFOME

Table 3 provides the CFP of biodiesel derived from blends of WFO and RCO, and their correlations are depicted in Figure 3. All CFP temperatures exhibit a downward trend as the RCO content increases in the BD samples. The findings indicate that blending WFO with RCO before biodiesel production reduces CFP temperatures in the resultant biodiesel samples. However, even with the addition of up to 50 vol % of RCO, the resulting fuel did not meet the requirements for suitability in regional climate conditions.

Table 3. Results for Method 1: CFP temperatures of WFO and RCO blends-based biodiesels

	RCO content (Vol %)	**CP**	**PP**	**CFPP**
100W0C	0	15	12	14
90W10C	10	15	7.5	13
80W20C	20	13	4.5	11
70W30C	30	12	4	9.5
60W40C	40	10	2.5	6
50W50C	50	9	0.5	5.5
0W100C	100	-3.5	-10	-7.5

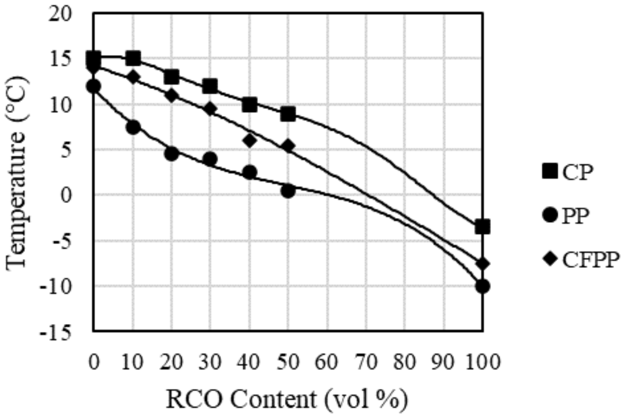

Figure 3. Effects of blending of WFO with RCO on the CFP temperatures

CP was linked to the proportion of RCO in the blend through an empirical fourth-order polynomial equation, represented by Equation 1. CFPP and PP, on the other hand, were associated with third-order polynomial equations, depicted by Equation 2. In these equations, X denotes the volume percentage of RCO, and T represents the temperature. The coefficients of these equations, along with their coefficients of determination (R^2), are provided in the last table of the study, Table 5.

$$T = a + bX + cX^2 + dX^3 + eX^4 + fX^5 \quad (1)$$

$$T = a + bX + cX^2 + dX^3 \quad (2)$$

Table 4. CFP temperatures of WFOME and RCOME blends

	RCOME content (vol %)	**CP**	**PP**	**CFPP**
100WFOME0RCOME	0	15	12	14
75WFOME25RCOME	25	14	6.5	8
50WFOME50RCOME	50	9	3.5	4.5
25WFOME75RCOME	75	3	-1	0
0WFOME100RCOME	100	-3.5	-10	-7.5

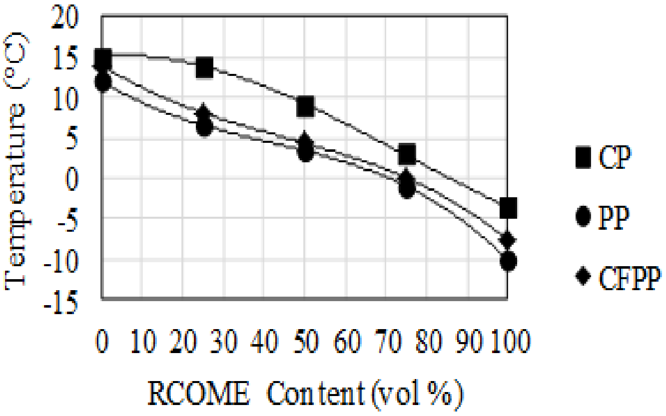

Figure 4. Effects of blending with RCOME on the CFP temperatures of WFOME

For Method 2, CFP temperatures of WFOME-RCOME mixtures are given in Table 4, and the effect of blending is presented in Figure 4. While there is a general trend of decreasing all CFP temperatures with increasing RCOME content, only blends consisting of 25 vol % WFOME and 75 vol % RCOME could be utilized throughout the entire year, except January and February. The other two blends, specifically 75WFOME-25RCOME and 50WFOME-50RCOME, were suitable for use only for six months, spanning from May to October.

All three CFP temperatures were correlated with the blend composition using an empirical third-order polynomial equation, as depicted in Equation 2. In this equation, X represents the volume percentage of RCOME, and T denotes the temperature. The coefficients of these equations and their corresponding R2 values, are provided in Table 5.

In Method 3, the CFP temperatures of WFOME - Commercial Petroleum Diesel blends were determined, and their relationship with commercial diesel content is illustrated in Figure 5. CP, CFPP, and PP tend to decrease with increased commercial diesel content. However, an exception was observed in the behavior of CP; up to 50% commercial diesel addition, CP remained constant, leading to an increase in the difference between CP and CFPP. A significant decrease in CP was observed when the concentration of commercial diesel was maintained between 70% to 90%. The difference between CP and CFPP converged to 2°C at 100% commercial diesel, similar to what was initially observed for the pure biodiesel. The current EN 590 gives six CFPP grades for various temperate climates. They change from Grade A to Grade F covering a range of CFPP from 5°C to -20°C. After determining CFPP at -4°C for the commercial diesel, it was concluded that the diesel purchased for blending corresponded to Grade C in the EN 590 standard.

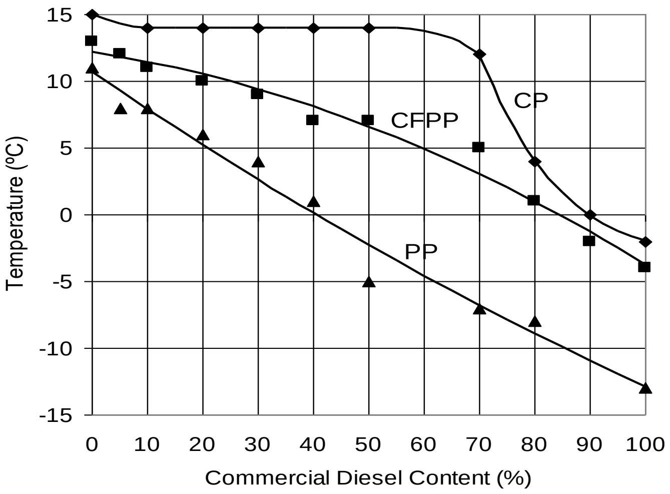

Figure 5. Effects of blending commercial diesel fuel on the CFPs of WFOME

Tang et al. (2009) found correlations between CP and PP with blend compositions using empirical second-order polynomial equations. However, they did not provide a correlation for CFPP. The CP curve depicted in Figure 5 can be associated with the blend composition below 70% using an empirical fifth-order polynomial equation and a heat capacity model for blends above 70% commercial diesel addition, as presented in Equation 3 and Equation 4, respectively. CFPP and PP were correlated with blend composition using empirical second-order polynomial equations, as shown in Equation 5. In these equations, X represents the commercial diesel content in percentage, and T denotes the temperature. The coefficients of these equations, along with their corresponding R^2 values, are provided in Table 5.

$$T = a + bX + cX^2 + dX^3 + eX^4 + fX^5 \quad \text{for } X \leq 70\ \% \qquad (3)$$

$$T = a + bX + cX^{-2} \quad \text{for } X \geq 70\ \% \qquad (4)$$

$$T = a + bX + cX^2 \qquad (5)$$

Bhale et al. (2009) noted that crystal growth inhibitors, also called pour point depressants, effectively reduce the PP of biodiesel. However, they typically do not influence the CP and CFPP at low temperatures. Figure 5 suggests that commercial diesel fuel can lower PP and CFPP in all blends. However, for reducing CP, blending becomes effective only when the concentration in the blend exceeds 70%.

Table 5. Coefficients of the empirical correlations for WFOME blends

Method	**CFP**	**Blend Content (vol %)**	**Correlation**	**Coefficients**						**R^2**
				a	***b***	***c***	***d***	***e***	***f***	
1	CP	0-100 % RCO	Eq. (1)	15.026	0.1173	-0.0177	0.0005	$-6x10^{-6}$	$2x10^{-8}$	0.9988
	PP	0-100 % RCO	Eq. (2)	11.722	-0.4576	0.074	$-5x10^{-5}$	--	--	0.9942
	CFPP	0-100 % RCO	Eq. (2)	14.184	0.1366	-0.0012	$4x10^{-6}$	--	--	0.9944
2	CP	0-100 % RCOME	Eq. (2)	15.036	0.0455	-0.042	$2x10^{-5}$	--	--	0.9996
	PP	0-100 % RCOME	Eq. (2)	11.986	-0.3095	0.0046	$-4x10^{-5}$	--	--	0.9999
	CFPP	0-100 % RCOME	Eq. (2)	13.979	-0.316	0.0039	$-3x10^{-5}$	--	--	0.9999
3	CP	≤ 70 % Diesel	Eq. (3)	14.999	-0.21131	0.01575	-0.00053	$1x10^{-5}$	$-1x10^{-7}$	0.99993
		≥ 70 % Diesel	Eq. (4)	-66.016	0.39324	247288	--	--	--	0.99992
	CFPP	0 -100 % Diesel	Eq. (5)	12.170	-0.06413	-0.00095	--	--	--	0.98902
	PP	0 -100 % Diesel	Eq. (5)	10.714	-0.28405	0.00048	--	--	--	0.98894

Conclusion

Utilizing waste frying oil (WFO) instead of virgin vegetable oil for biodiesel production offers an effective means to reduce raw material costs while also addressing the issue of waste oil disposal. The current study produced biodiesel from WFO and RCO using a base catalyst transesterification reaction. Biodiesel derived from WFO exhibited a higher waxing temperature than commercial diesel fuel and RCO-based biodiesel. The biodiesel produced from WFO demonstrated poor cold flow properties, with critical parameters for low-temperature applications: CP, PP, and CFPP temperatures measured at 15°C, 11°C, and 13°C, respectively. These poor cold flow characteristics restrict the use of pure WFO-based biodiesel from May to October in Nicosia. However, blending biodiesel with commercial diesel fuel can enhance all three properties, enabling suitable blends for winter use.

Scientific Ethics Declaration

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

Acknowledgements or Notes

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