

Experimental Study on the Distillation Capacity of Alcohol-Gasoline Blends

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Abstract. The paper objective is to highlight the consequences of adding different alcohols in gasoline on the distillation characteristics of these blends. Changes of the distillation parameters (t_i , t_{10} , t_{50} , t_{90} , t_f , E70, E100, E150) have been evaluated and, also, the evolution trends of the distillation curves for different alcohol added in mixture with the gasoline have been estimated. Several types of gasoline sold on the market and methanol, ethanol, i-propanol and butanol were used during the experiments and the corresponding distillation curves have been analyzed. The alcohol fraction in mixtures varied between 5 and 20%. Double blends with alcohol added in gasoline and triple blends with two alcohols added in gasoline were used. The comparison of the distillation curves of the mixtures was done with respect to that of pure gasoline. It was specified how the values of the distillation parameters, E70, E100 and E150, were set within the limits of EN 228. The distillation was made on 100 ml of fuel and the measurements were made on each 10 ml of fuel transformed into vapor state and then condensed. The influence of the alcohols present in these mixtures was manifested by the changes in the shape of the distillation curve. The butanol influence on the distillation temperatures was found lower than that of ethanol, because the physicochemical properties of the butanol are closer to those of gasoline. The molecules of alcohols actively interact with the fractions of gasolines, their combination leading to a conjugate effect and to a modifying the distillation parameters values. The variation of these parameters depends on the alcohol fraction in the mixture.

1. Introduction

The current resources of fossil fuels are limited; they are estimated to end in about 45 years. There is a need to look for alternative fuel sources, especially as the world's population will grow and fuel consumption will increase. At the same time, the pollution level of the planet has increased significantly during the recent years, and both the European and world level are pursuing the implementation of increasingly severe environmental standards. An important contribution to the global level of pollutants emitted into the atmosphere is represented by the pollutant emissions resulting from the combustion of fuels in the internal combustion engines (i.c.e.). That is why they were limited for car manufacturers by regional regulations. The transport sector is ranked third by the European Union in terms of greenhouse gas emissions. In this context, the use of alcohols as independent fuel or mixed with fossil fuels represents a direction of great interest for the fuel industry [1]. Another argument in using alcohols is that some of them can be obtained from the fermentation of



biomass that is a renewable source. It also leads to a decrease in dependence on oil-holding countries and changes geo-political strategies.

It has been admitted since back the '80s that the methanol and ethanol are accepted, technically speaking, for use on i.c.e. and, in time, researches has focused on other alcohols such as propanol, butanol, pentanol. A history of the use of gasoline-alcohols mixtures is presented in [2].

Some researches aimed at studying combustible mixtures with large shares of alcohols (5%-85%) in mixture [2, 3], others investigated narrower registers (5%-20%) [4, 5, 6].

In the gasoline sold on the Romanian market, the share of alcohols is restricted to a few percentages, alongside other oxygenated compounds. Standard EN 228 makes the following specifications found in the blending formula from the technical specifications of gasoline: it limits the oxygenated compounds content to 2.7% m/m, methanol to 3% (v/v), ethanol to 5% (v/v) and it requires a minimum of 4.5% (v/v) biofuel.

The alcohols used in mixture with the gasoline [3,7] have different properties from those of it. In table 1, compared to gasoline, the most important characteristics of alcohols that were used in this study are presented.

The high octane number of alcohols leads to the improvement of the ON of the gasoline to which they are added. This way higher compression ratios or larger spark advances can be used, which leads to higher engine efficiency [8]. Oxygen in the alcohols' molecule reduces the minimum air for complete combustion and allows changing the ignition limits of the mixture.

The high latent heat of vaporization of alcohols leads to the reduction of the temperature at the end of the intake process, allowing the increase of the amount of substance evolving during the cycle in the cylinder. The effective power downward trend due to the lower calorific power of alcohols can be recovered by increasing the fuel consumption. This will require an enlargement of the fuel tank. The vapor pressure of alcohols; is lower than that of gasoline; consequently, it makes more difficult the cold start of the engine, a disadvantage that demands the adoption of some specific constructive solutions. The higher the percentage of added alcohol, the more extensive constructive adaptations are. FFV-Flexible Fuel Vehicles are vehicles tailored to various amounts of alcohols [9], capable to regulate the engine operation in correlation with the measured alcohol content. Thus, many vehicles have been equipped with engines that can operate with gasoline and ethanol from 0% to 85% without constructive changes [10].

Although the percentage of ethanol may vary over a wide range, the best results for the exploitation characteristics have been reported for percentages up to 20%.

In terms of pollutant emissions [2, 11], when using mixtures of gasoline and alcohols, HC and CO emissions decrease while for NO_x and volatile organic compounds involved in smog formation increases have been reported [7,12 13].

Regarding the fuel consumption, although oxygenated fuels have a lower calorific power than gasoline, some experiments showed similar consumption expressed in l / km and usually lower when expressed in units of energy (MJ / km).

The benefits of using alcohols in mixture with gasoline are maximum around the percentage of 20%. The corrosive effects of alcohols also lead to limitations of the percentage added to the blend [4,5,6,14].

The fractional distillation is based on heating the liquid to the boiling point when it vaporizes and then condensing it back into the liquid state. In the case of gasoline, which consists of hundreds of fractions, each fraction has its boiling point, and thus a temperature range for boiling is obtained for gasoline. The distillation curve expresses the percentage of fuel that distils up to a certain temperature. Thus, the first distil the light fractions, followed by the medium ones, then the heavy ones. By its specific parameters ($t_i, t_{10}, t_{50}, t_{90}, t_f$, E70, E100, E150, total distilled percentage and the amount of residue), the distillation curve provides information on fuel volatility that affects the exploitation, transport and storage characteristics.

The parameter t_i - the initial distillation temperature and t_{10} - the temperature at which 10% of the fuel volume distils characterize the cold start engine's capability and behavior. The T50 has an influence on

engine warm-up time and on its operating stability. The parameter T90 is related to the combustion characteristics of fuel, influencing the complete burning, the fuel consumption, the engine wear, and deposits inside the engine.

E70, E100 and E150 represent the percentage of liquid that distilled up to 70, 100 and 150 °C respectively [5]. Tf-final distillation temperature is the maximum temperature recorded during the distillation process.

The addition of alcohols in gasoline leads to the modification of some characteristic parameters of the distillation curve of the mixture. The study aimed to highlight the influences of different alcohols (M-methanol, E-ethanol, iP-isopropanol and B-butanol) added in varying proportions to the distillation characteristics of the mixtures.

The quality of the produced and traded gasolines is controlled by standards such as EN 228, standard which compels the distillation parameters (t10, t50, t50, tf, E70, E100, E150) within certain limits.

2. Materials and methods

There have been used the ON 95 pure gasoline sold on the market and blends of gasoline with methanol, ethanol, i-propanol and butanol, the alcohols being added in proportions ranging from 5 to 20% (v / v). There have been used double mixtures, gasoline + an alcohol and triple mixtures gasoline -80% (v/v) + two types of alcohols (E+iP, E+B and iP+B) 20% (v/v), meaning 10% (v/v) for each of the two alcohols.

The fractional distillation was carried out under ASTM 86 conditions. Samples of 100 ml of gasoline and gasoline-alcohol blend were used. Heating was done at a rate of 5ml /min. Several determinations were performed for the same type of sample (Figure 1) and the average values of the measurements were used.

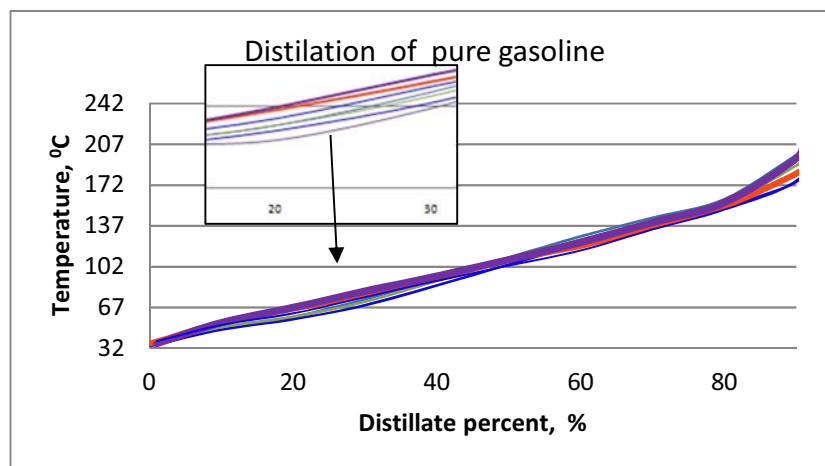


Figure 1. Several distillation curves for pure gasoline

3. Results and comments

The values obtained for the characteristic parameters of the fractional distillation are shown in table 1. The obtained distillation curves are shown in figure 2. The addition of alcohols led to changes in the distillation curves; a plateau area shows up close to the “steam point” of the alcohol.

In the case of addition of 20% methanol to the mixture (M20), the plateau area in the distillation curve is below the M100 pure methanol distillation point (64,5°C). Lower values are obtained for the distillation temperature starting from more than 10°C below the methanol distillation temperature. The size of this range extends over a longer, almost double range from the 20 percent added methanol, which is higher than the

volumetric proportion of methanol in the blend. This is due to the interaction of methanol molecules with mild HC, leading to the formation of azeotropes, with synergistic effects of increasing volatility [16].

Table 1. The distillation parameters of several alcohol-gasoline blends

Parameters	Gasoline	Gasoline blended with 20% alcohol						
	Free alcohol	M20	E20	iP20	B20	E10+ iP10	E10+ B10	iP10+ B10
t_i , °C	39	40	40	40	39	38	40	38
t_{10}	53	53	54	57	60,5	55	57	55
t_{50}	100,5	68	73	78	102,5	74	82	90
t_{90}	169,5	168	158	153,5	163,5	152	159	158
t_f	190	188	170	182	195	179	188	183
Distillate %v/v	95	95	93	96,5	97	95	97	97
Residuum %v/v	2	2	1	1	1,5	1,5	1,5	1,5
E70, %v/v	23,5	51,5	39,5	30	18	38	29	35
E100 %v/v	50	56	76	63	49	68	60	65
E150 %v/v	85,5	79	87	78	85	80	85	86,2

M=methanol, E=ethanol, iP=i-Propanol, B=butanol

M20=20% methanol +80% gasoline; E20=20%ethanol+80%gasoline;...

E10+ iP =10%ethanol+10%i-propanol+80%gasoline;...

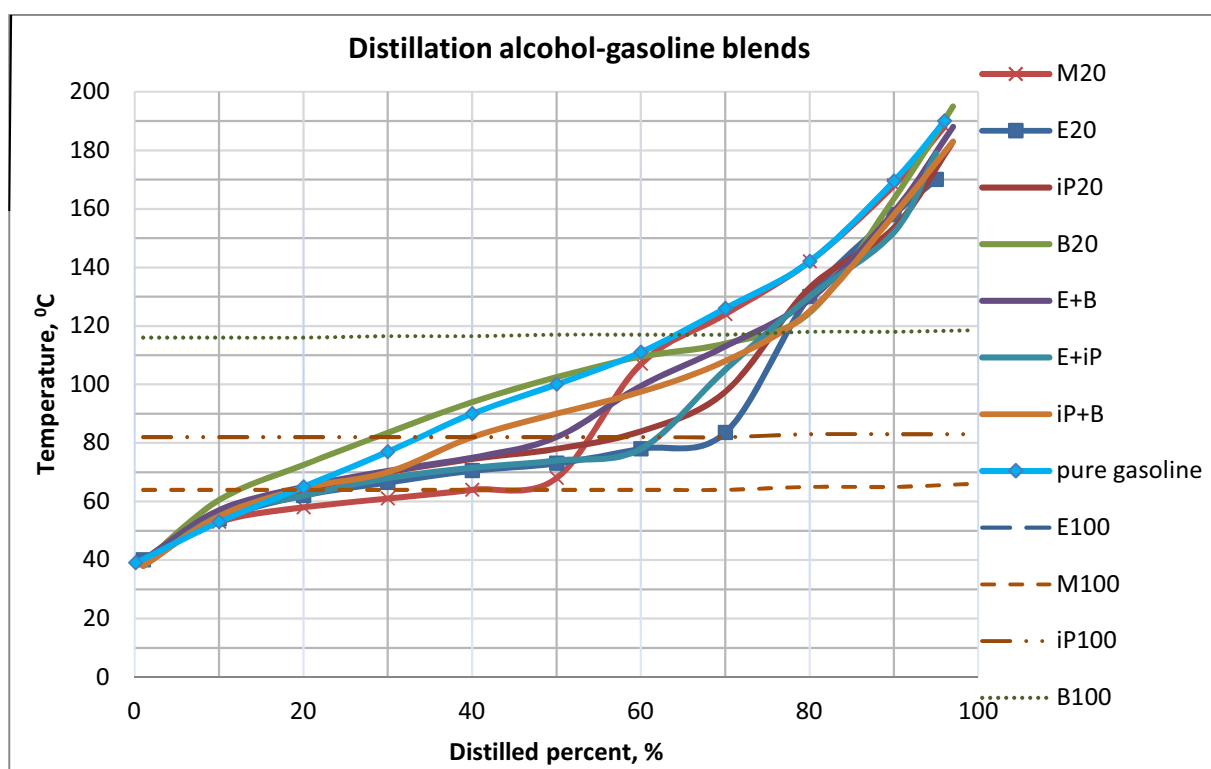


Figure 2. Distillation curves for pure gasoline, pure alcohols and alcohol gasoline blends

The M20 mixture records an E70 value (51° C) above the limit set by EN 228 (20°-50°C) and values that meet the requirements of the E100 (46°-71°C) and E150 (> 75°C) standards (Figure 3) [17].

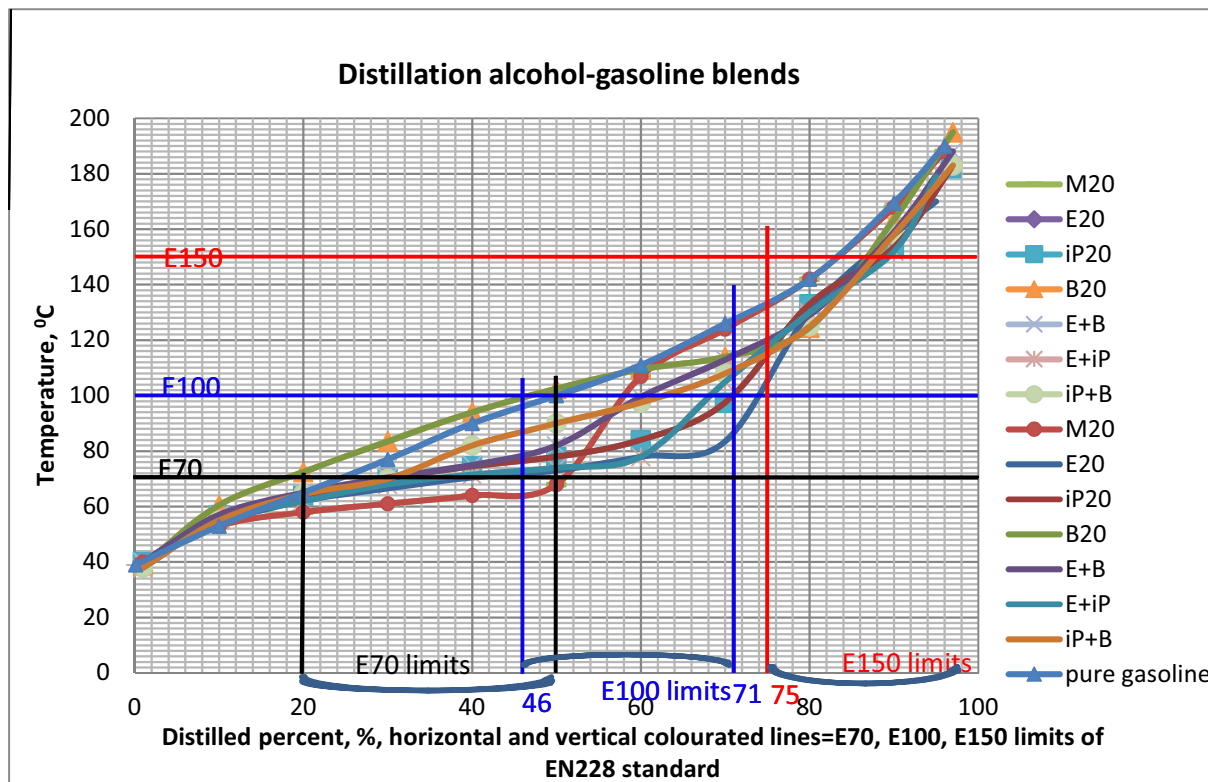


Figure 3. Distillation curves for alcohol-gasoline blends and the Standard EN 228 limits for volatility.

The horizontal and vertical colored lines represent the E70, E100, E150 limits of EN228 standard. The minimum value for t₅₀ (68°C) and the maximum value of t₉₀ (189°C) belongs to M20.

The E20 mixture also shows a distillation curve of a higher stretch on the axis of the distillate than methanol. The plateau is manifested at a higher temperature than the methanol mixture, justified by the ethanol distillation point (78°C) higher than that of methanol. For ethanol, the distillation curve shows the highest deviation from the pure gasoline distillation curve.

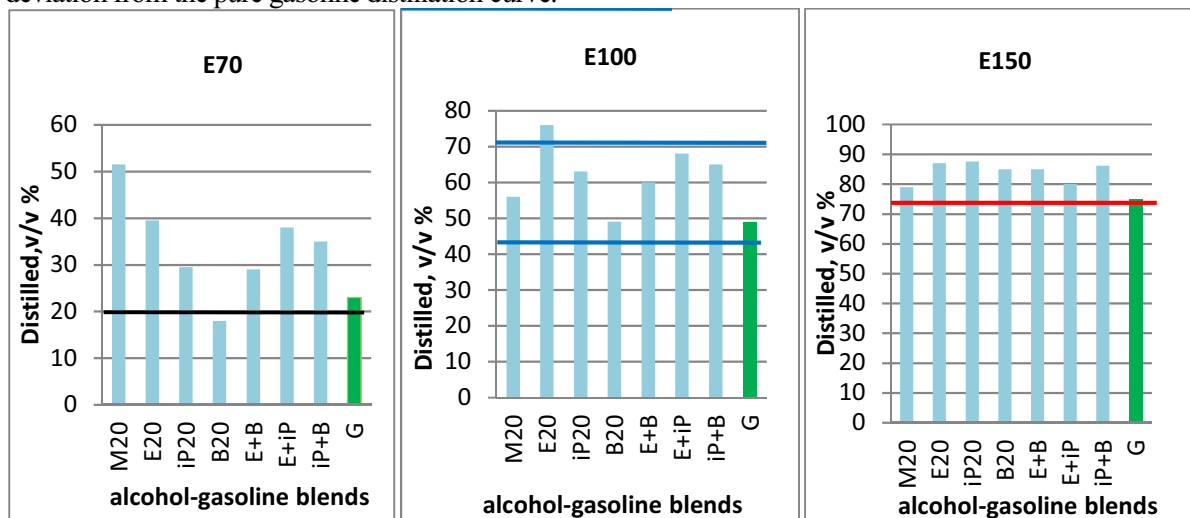


Figure 4. The values of the E70, E100 and E150 parameters for the alcohol gasoline blends
The horizontal colored lines = the limits of the EN 228 Standard

As in the case of M20, the plateau of distillation curve of the mixture E20 is manifested at a lower temperature than the distillation of ethanol. Near the 110°C temperature, the distillation curve of the mixture with methanol returns to the characteristic values of the pure gasoline distillation curve.

In this case also, the interaction of ethanol molecules with light and medium fractions of gasoline and the formation of azeotropes take place. The E20 blend has E70 and E150 within European limits, but it exceeds the recommended range for the E100 (46°-71°C, Figure 3), showing greater volatility (74°C, Figure 4).

The mixture with i-propanol, iP20, meets the volatility requirements for the E70, E100, E150. The degree of variation of the mixture distillation curve compared to that of the gasoline is lower than that of M20 and E20.

The B20 distillation curve deviates from that of pure gasoline in both light and heavy hydrocarbons. In the first case, it has higher values, while in the second case its values are lower. The interaction of butanol with light HC molecules raises the B20 distillation temperature curve as against to the gasoline's while with the heavy HC the butanol causes the distillation temperature curve to decrease. The distillates of B20 blends are situated within the E100 and E150 volatility limits, but they are below the lower limit of the recommended range for E70 (Figure 4).

Notable for triple blends with two alcohols is that they all fit into the recommendations of the EN 228 Volatility Regulation. The deviations of the distillation curves are greatly attenuated. The largest change in the distillation curve compared to pure gasoline is shown in the E + iP mixture while in the case of iP + B mixture the deviation is the smallest. The initial distillation temperatures have very little variation from that of pure gasoline. The temperature t10 recorded the lowest value for the M20 mixture and the highest for B20.

T50 temperature has the lowest value for M20, followed by E20 and it is the highest for B20. T50 for the triple E + iP mixture is only 1 degree above the E20 mix.

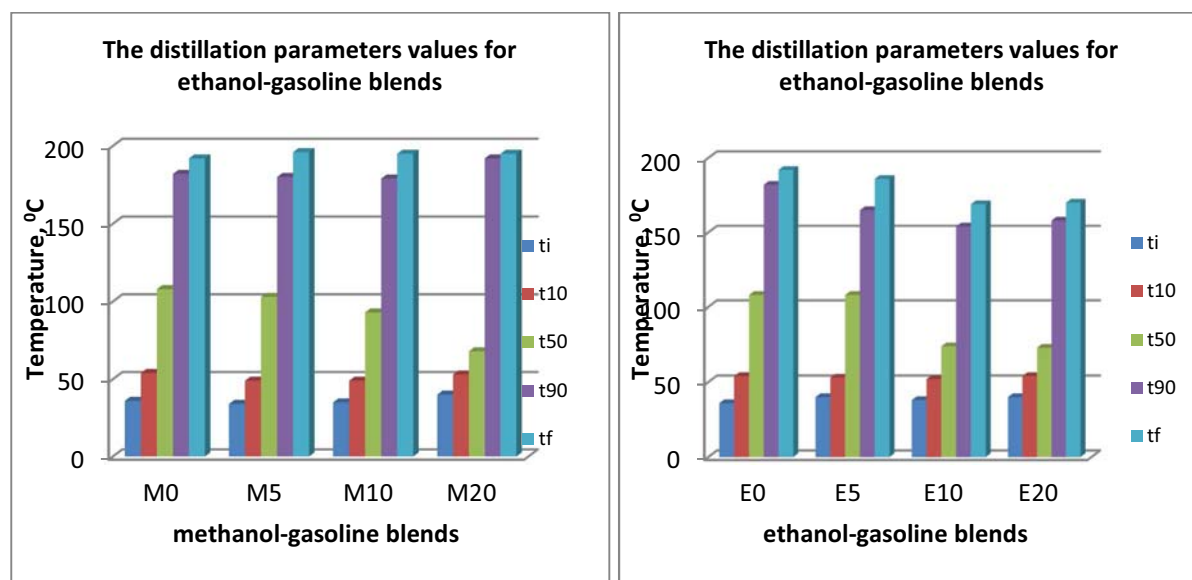


Figure 5. The variation of the distillation parameters ti,t10,t50,t90,tf, for the methanol-gasoline and ethanol-gasoline blends with the percentage of alcohol.

The temperature t90 has the lowest value for the triple E + iP mixture, very close to the iP20, and the highest value for B20, justified by the highest distillation point of pure butanol alcohols.

The distillations parameters ti,t10,t50,t90,tf, for each alcohol-gasoline mixture varies with the percentage of alcohol. Figure 5 presents the variation of the distillations parameters ti,t10,t50,t90,tf, for the methanol-gasoline and ethanol-gasoline blends with respect to the percentage of alcohol. In the case of methanol, there is an influence on t10 and t90 and, in the case of ethanol, it is recorded on t50, t90 and tf.

4. Conclusions

The double blends of pure gasoline with alcohols have modified the distillation curves compared to pure gasoline, the shape of the curve presents a plateau, whose size is proportional but greater than the percentage of added alcohol. The largest deviation was recorded for the E20 mixture.

E70 for blend B20 does not fall within the limits required by EN 228, being below them.

Mix E20 has a value for E100 that exceeds the maximum value allowed. The M20 mixture showed a higher volatility of the light fractions, the value of the E70 parameter exceeded the upper limit mentioned in the EN 228 standard.

In the case of triple blends with two alcohols, the distillation curves deviated less from those of pure gasoline. In all cases the characteristic values of the volatility of the triple blends were within the ranges specified in the Regulation.

5. References

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