

ÁREA TEMÁTICA: Área 3: Reciclagem

SIMULATION TOOLS FOR THE ASSESSMENT OF ADVANCED THERMAL TREATMENT OF MSW – GASIFICATION CODE

Jackson costa da silva (*Jacksonc.silva21@gmail.com*), Carlos Alberto Gurgel Veras (*gurgel@unb.br*), Antônio Cesar Pinho Brasil Jr. (*brasiljr@unb.br*)

Energy and Environment Laboratory - Mechanical Engineering Department university Campus Darcy Ribeiro - University of Brasília

ABSTRACT

The landfill near downtown Brasilia was shut down some years ago. The site was estimated to have near 19,000,000 tons of mixed waste materials. Strategic studies are being carried out for the energetic utilization of the stored recoverable energy. Advanced conversions technologies for municipal solid waste are based on either, pyrolysis or gasification. In this work we present a novel thermochemical equilibrium model for the gasification of MSW. In most instances the producer gas has to be cleaned for particle matter and tar extraction before end-use application. We thus proposed a two-step conversion pathway in which carbonization of MSW is performed in a stand-alone equipment followed by gasification of the derived charcoal for low tar producer gas. A thermal equilibrium code was developed and applied to investigate MSW-char gasification performance parameters for heat and power generation. Code predictions confirmed the improved quality of the syngas when MSW-char is used as the feedstock. Low temperature steam gasification of the derived charcoal further increased the quality of the syngas for Fisher-Tropsch synthesis and heat engine applications by virtue of its high content of hydrogen and carbon monoxide. An integrated char gasification power engine cycle would produce 7,1 MW of heat and power from the gasification of 9.2 metric tons per hour of MSW-char.

Keywords: Environmental remediation; Brasília landfill; Gasification modeling.

Nomenclature

ER_g	Gasification Equivalence Ratio	ASH	Ashes
$G_{f,i}^0$	Specific free energy of Gibbs formation (kJ / kmol)	C	Carbon
g	Molar Gibbs free energy (kJ/kmol)	CO	Carbon monoxide
h	Molar specific enthalpy (kJ/kmol)	CO_2	Dioxide
HHV	Higher Heating Value (kJ/kg)	CH_4	Methane
$(h_{f-298}^0)_w$	Molar Enthalpy of formation of species w (kJ/kg-K)	H	Mono atomic hydrogen
L	Auxiliary equation	H_2	Diatomic hydrogen
MW_w	Molecular weight of species w (kg/kmol)	O	Mono atomic oxygen
m_{water}	Mass of water	N	Mono atomic nitrogen
m_{ox}	Mass of oxidizer (air)	N_2	Diatomic nitrogen
m_{ash}	Mass of ash	SiO_2	Silica
$m_{ox,st}$	Stoichiometric oxidizing mass	Greek symbols	
m_{fs}	Mass of biomass	β	Moles of ash
m_{ar}	Air mass	α	Moles of water
n_w^i	Input mols of species w	γ	Air N_2/O_2 ratio
n_w^o	Output mols of species w	Indexes	
n_{CC}	Carbon conversion efficiency	i	Input
		o	Output

P	Total pressure	Subscripts	
P_{CH_4}	CH ₄ partial pressure		CC Carbon conversion
T	Temperature (K)		
X_w	number of atoms of chemical component w		

INTRODUCTION

The Paris Agreement, signed by the majority of the countries, aimed to reduce greenhouse gases leading to a hold of the global mean temperature below 2.0 °C relative to the pre-industrial era. In a regional context, 18 countries from South America established specific goals in order to increase the share of renewable energies sources to their electricity matrix (Washburn and Romero, 2019). Brazil, along with Mexico, Chile and Uruguay are leading this course since 2010. As for Brazil, electricity production is mostly renewable. Regardless of such favorable characteristic, the country has set a 35% decrease in its emissions before the year 2026, based on the levels of 2005.

In terms of electricity the proposed target for 2023 suggested an 86% nationwide power production from renewable sources, in particular that from agricultural waste, which, for the 2015 figures amounted 50 MToe. The contribution of the sector may reach 165 MToe by the year 2050 (EPE, 2018). Converting this huge amount of primary energy into electricity claims advanced thermal treatments, such as pyrolysis and gasification of biomass and Municipal Solid Waste (MSW). These feedstocks, however, should be employed when solar and wind are less competitive in terms of US\$/kW, mainly for the production of biofuels, chemicals and alternative materials (IEA Bioenergy, 2015). MSW and biomass are readily available for most of the time in a year cycle, as opposed to wind and solar, and would help in stabilizing a multisource electricity production system.

Steam gasification of carbonaceous materials produces a syngas with increased calorific value and high concentrations of hydrogen and carbon monoxide mostly due to the absence of nitrogen (Bartocci et al., 2018). Syngas with such characteristics is a valuable feedstock in the production of hydrocarbons from Fisher-Tropsch synthesis. The absence of nitrogen in the fuel gas also allows the implementation of carbon capture and storage technologies in integrated gasification gas turbine/engines cycles (Krieger et al., 2015).

Tar concentration in producer gas for engine cycle applications is limited to about 100 mg/Nm³ (Milne et al., 1998). Staged gasification technologies have been proposed to circumvent complex gas cleaning systems for biomass gasification (Bui et al., 1994; Bhattacharya et al., 1999; Jaojaruek et al., 2011; Gómez-Barea et al., 2013).

In a recent study our research group proposed a different type of staged gasification technology for low tar producer gas (Miranda et al, 2020). The system is based on specific processes taking place in two standalone reactors. First, the biomass or MSW is thermally degraded in a carbonization reactor. In a following process, gasification of the derived char occurs in a single stage, regardless of the reactor's technology, fixed bed, fluidized bed or any other system configuration. By such means, the producer gas is virtually absent of heavy condensable hydrocarbons (tar). Straightforwardly, the downstream gas cleaning system can be of low complexity and cost. Figure 1 shows the two-step biomass and MSW conversion plant for low tar gas production. As it can be seen, both processes take place in two specialized plants, each having the highest level of maturity (TRL = 9) in terms of technology. As such, the system is integrated from off-the-shelf components. Another interesting feature of the proposed thermal conversion process lies on the possibility of using linear Fresnel systems to produce saturated steam for the carbonization plant. The superheating of the steam would take place in the heat recovery exchanger placed before the gasifier.

Following the proposed thermal conversion pathway, our research group is currently developing enhanced simulations tools to assess the performance of integrated MSW gasification gas engine cycle and cogeneration plants. This paper thus presents a novel thermal equilibrium model for

gasification reactions of carbonaceous feedstocks. The present model will be further coupled to a pyrolysis and heat engine models applied to advanced thermal treatment of municipal solid waste

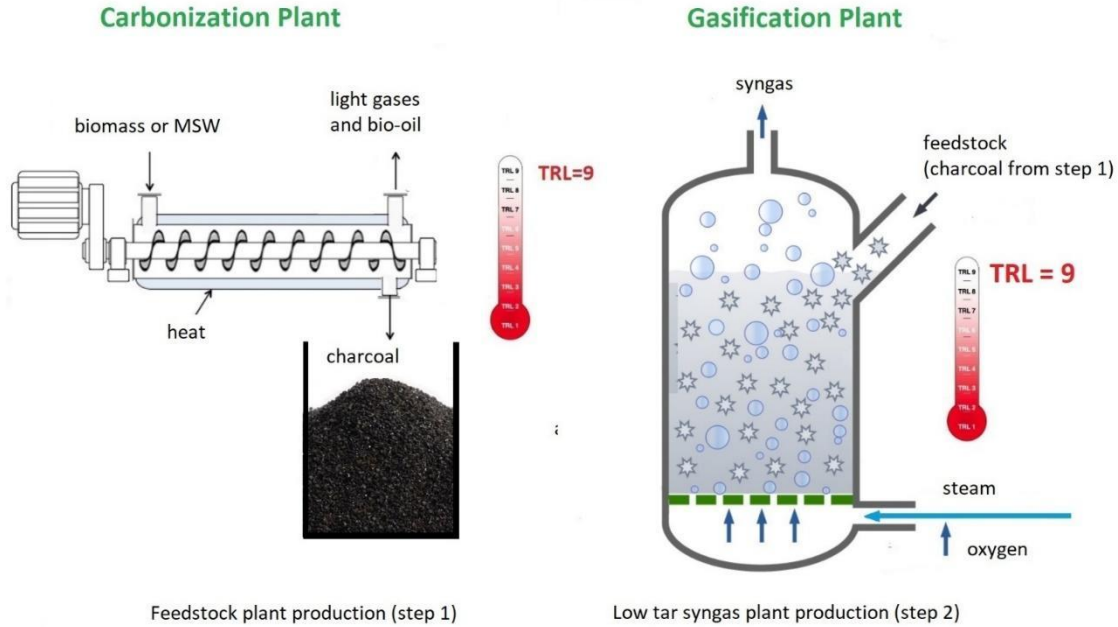


Figure 1: Two-step conversion of carbonaceous feedstock for low tar gas production.

CARBONIZATION OF BIOMASS AND MSW

Thermal degradation of biomass and MSW produce bio-oil, charcoal and light gases, at different proportions, depending on process parameters such as the heating rate, maximum temperature, holding time and the composition of feedstock. To some extent, the carbonization process can be designed to produce charcoal with prescribed levels of H/C and O/C ratios, as shown in Fig. 2. The low concentrations of hydrogen and oxygen in charcoal reduces the formation of tar throughout the gasification process. Also, charcoal has improved storage characteristics and much higher heating value and energy density than the original feedstock, whether biomass or MSW. The region which characterizes the MSW in Fig. 2 was taken from Phyllis2 -Database (2020).

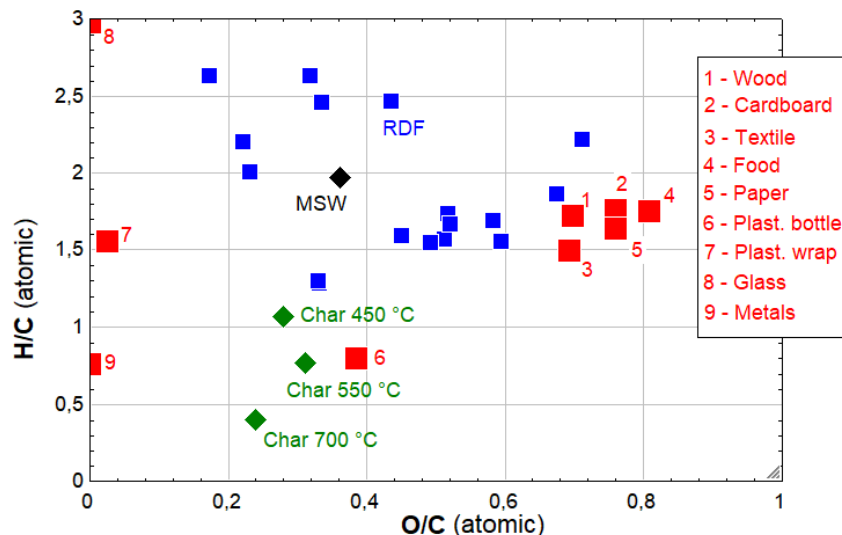


Figure 2: Van Krevelen diagram for common materials of MSW and upgraded fuel (RDF and char).

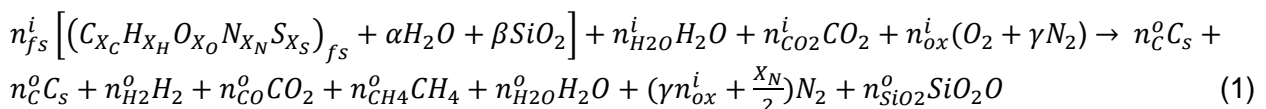
As it can be seen, carbonization temperature in the range of 450-700 °C reduces the H/C and O/C atomic ratios to as low as 0.4 and 0,22, respectively. These levels are deemed adequate for low tar syngas production for heat engine applications and Fisher-Tropsch synthesis. In the region of 300 to 450 °C, most of the cellulose and hemicellulose in the feedstock have been thermally degraded. For the proposed conversion pathway, the thermal degradation process has to be designed to maximize charcoal yields. For that, the suggested process parameters are: low heating rate and pyrolysis temperature not exceeding 700 °C at some predefined holding time. These process parameters can be obtained from TG analysis, for instance. Low heating rates and mild maximum pyrolysis temperatures are fulfilled by most of the off-the-shelf carbonization reactors available in the market. In this work, the proposed two-step conversion pathway which can be applied to the solid fuel waste deposited at the “Estrutural” landfill located near downtown Brasilia. The site had been operating for 50 years and has about 19,724,915 tons of waste. Preliminary sampling from the landfill indicated the waste is comprised of 26% cellulosic material, 23% plastic, 27% water, 21% inert and 3% organics.

Charcoal production from the pyrolysis of waste mixture would come, almost exclusively, from the cellulosic fraction. Sorum et al. (2001) reported an average of 24.7% in charcoal yields from TG analysis of the cellulosic fraction of MSW up to 450 °C maximum temperature. At 10 °C/min heating rate. Most of the feedstock degradation occurred between 250 and 400 °C and maximum weight losses in the range of 355-371 °C. As for the plastic fraction, charcoal yields are negligible. Based on these figures, we could produce about 1,266,000 tons of charcoal from the slow pyrolysis of the MSW from the “Estrutural” landfill.

GASIFICATION MODEL

Gasification Reaction

For the present work, the gasification reaction of a carbonaceous material is given by



In Eq. (1), the feedstock composition accounts for the presence of water and ash, through parameter α and β , respectively. Gasification agent is composed of a mixture of steam, carbon dioxide, oxygen and nitrogen at prescribed composition, after adjusting the stoichiometric number of moles for each substance. Both, the feedstock and specific gasification agents can be introduced into the reactor at any given temperature.

Conservation of chemical elements (C, H, O, N, S) is given by

$$n_{CO}^o + n_{CO_2}^o + n_{CH_4}^o + n_C^o - n_{fs}^i X_C - n_{CO_2}^i = 0 \quad (2a)$$

$$2n_{H_2}^o + 2n_{H_2O}^o + 4n_{CH_4}^o - n_{fs}^i X_H - 2n_{fs}^i \alpha - 2n_{H_2O}^i = 0 \quad (2b)$$

$$n_{CO}^o + 2n_{CO_2}^o + n_{H_2O}^o - n_{fs}^i X_O - n_{fs}^i \alpha - n_{H_2O}^i - 2n_{CO_2}^i - 2n_{ox}^i = 0 \quad (2c)$$

$$n_{N_2}^o - \gamma n_{ox}^i - (n_{fs}^i X_N)/2 = 0 \quad (2e)$$

$$n_{SiO_2}^o - n_{fs}^i \beta SiO_2 = 0 \quad (2f)$$

Only Eq (2a) to Eq. (2c) need integration. The output mass of nitrogen and sulfur can be obtained straightforwardly by the composition of the biomass and the gasification agent.

The as received composition of the feedstock (m_{ar}), its ash (ASH) and moisture contents (MC), in terms of percentages, are used to infer the relative number of moles of H_2O and SiO_2 , represented by α and β . For a given mass of as received feedstock (m_{fs}), α and β are estimated as follows

$$\alpha = \frac{m_{water}}{MW_{H_2O}} \quad (3)$$

$$\beta = \frac{m_{ash}}{MW_{ash}} \quad (4)$$

We thus need to infer the mass of water, ash and dry feedstock from the as received analysis. The mass balance for the main components are then

$$m_{fs} = m_{ar} - m_{water} - m_{ash} \quad (5)$$

In Eq. (5) the mass of ash and moisture is calculated from their contents (%) in the as received feedstock

$$m_{ash} = \frac{ASH}{100} m_{fs} \quad (6)$$

$$m_{water} = \frac{MC}{100} (m_{fs} + m_{ash}) \quad (7)$$

The output of unconverted solid carbon may be given by a predetermined efficiency (n_{CC}) of conversion such as

$$n_C^o = n_{fs}^i X_C (1 - n_{CC}) \quad (8)$$

Process equivalence ratio (ER) is given by

$$ER = \frac{(A/F)_{stoic}}{(A/F)_{actual}} \quad (9)$$

For a non-prescribed gasification temperature, the equation of energy needs to be solved. Assuming gasification as a process without work and heat interactions the enthalpy of the products should be equal to the enthalpy of the reactants. The enthalpy of the products is defined from the equilibrium composition of the syngas (second law). The absolute enthalpy of the reactants is made with the contribution of the sensible and formation parts of the feedstock and the gasification agent. The enthalpy of formation of the feedstock can be calculated by (Mendiburu et al., 2014)

$$(\underline{h}_{f-298}^o)_{fs} = HHV(MW_{fs}) + (\underline{h}_{f-298}^o)_{CO_2} + \frac{X_H}{2} (\underline{h}_{f-298}^o)_{H_2O(l)} \quad (10)$$

where

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211ASH \quad (11)$$

The enthalpy of the remaining substances at any given temperature and pressure are obtained directly from the JANAF thermochemical tables inserted in the Engineering Equation Solver code EES, 2020).

○ Numerical Modeling

The composition of the gasification products is obtained through minimization of the Gibbs free energy giving by

$$g = \frac{G}{RT} = \sum_{i=1}^N n_i^g \left[\frac{G_{f,i}^0}{RT} + \ln \frac{n_i}{n_t} + \ln \frac{P}{P_0} \right] + \sum_{i=N+1}^L n_i^{l,s} \frac{G_{f,i}^0}{RT} \quad (12)$$

For the syngas species concentration estimates, we follow the scheme proposed in Mendiburu et al. (2014), based on the minimization of the objective function, Eq. (12), using Lagrange multipliers. The sum of the mass conservation of every chemical element after multiplied by the Lagrange multipliers gives the following auxiliary equation

$$L = \sum_{j=1}^K \lambda_j \left[\sum_{i=1}^M (a_{ji}n_i)_p - (b_j)_R \right] = 0 \quad (13)$$

Another auxiliary equation relates Eq. (12) and Eq. (13) through

$$H = g - L \quad (14)$$

The minimization is obtained by the partial derivative of H in relation to the Lagrange multipliers and the number of moles of each species, that are equally null, in the gas product of the reaction. The problem is therefore, find the product gas composition that satisfies the following equation

$$\left[\frac{G_{f,i}^0}{RT} + \ln \frac{n_i}{n_t} + \ln \frac{P}{P_0} \right]_g + \left[\frac{G_{f,i}^0}{RT} \right]_l + \left[\frac{G_{f,i}^0}{RT} \right]_s - \frac{\partial}{\partial n_i} \left(\sum_{j=1}^K \lambda_j \left[\sum_{i=1}^M (a_{ji}n_i)_p - (b_j)_R \right] \right) = 0 \quad (15)$$

In many thermochemical equilibrium codes, the amount of methane in the syngas is prescribed. In this work, we employed a correlation proposed in Mendiburu et al. (2014), for the number of moles of methane in the producer gas

$$n_{CH_4}^0 = \frac{P_{CH_4}}{100} \left[\frac{\eta_{CC} X_C + \frac{X_H}{2} + \frac{m_{water}}{MW_{H_2O}} + \frac{X_N}{2} + \gamma n_{ox}^i - n_{H_2O}^0}{1 + \frac{P_{CH_4}}{50}} \right] \quad (16)$$

Solution Algorithm

The main set of equations Eq. (1) to Eq. (16) was implemented in the EES code (Fig. 3).

CO	23.63	21.62
H ₂	18.7	19.92
CO ₂	11.4	11.58
N ₂	43.87	45.20

After the validation process, the code was then applied to the gasification of MSW and some MSW-chars produced at different carbonization temperatures. Thermal equilibrium code predictions of gasification of MSW and the three chars derived from municipal solid waste pyrolysis are shown in Table 2. Chars were obtained after pyrolysis at 450, 550 and 700 °C. Their relative H/C and O/C ratios can be seen in Fig. 2, along with the MSW extracted from the Phyllis2 database.

The performance of the feedstocks after gasification was investigated based on the following input parameters:

- Gasification of MSW with air preheated to about 580 °C;
- Gasification take place at sea level pressure;
- Steam to dry charcoal ratio, by mass, was set to 0.10;
- Moisture and ash content of char were 3.0% and 18%, respectively;
- Moisture and ash content of MSW were 6.16% and 15.78%, respectively
- Optimized equivalence ratio was in the range of 2.0 to 3.5;
- Producer gas cooled to 25 °C;
- % vol. of CH₄ in the producer gas calculated with the help of Eq. (19);
- Unconverted char equivalent to 5% of dry feedstock input;
- MSW char (700 °C) steam gasification at 927 °C.

As it can be seen from Table 2, the cold gas efficiency for MSW and the chars are in the range of 71 to about 77% with lower heating value, in volumetric basis, varying from 3,396 to 4,466 kJ/Nm³. The results from Table 2 show that, gasification of MSW-char gives a syngas with higher heating value slightly inferior to the gasification of the parent feedstock. H₂ and CO concentration for air gasification is in the range of 7-20% and 15-21%, respectively. Such gas composition was obtained with reaction equivalence ratio from 2.1 to 2.7, for which, gasification temperature varied from 570-685 °C.

Table 2: Gasification performance parameters of MSW and MSW-chars.

	CH _{1.97} O _{0.36}	CH _{1.1} O _{0.28}	CH _{0.77} O _{0.3}	CH _{0.4} H _{0.24}	
	(MSW)	(Char 450 °C)	(Char 550 °C)	Air	Steam
ER [-]	2.7	2.3	2.2	2.12	infinite
T [°C]	685	596	577	570	627
Gas composition, vol. %					
CO	15.51	15.68	16.41	20.29	39.64
CO ₂	9.42	11.86	13.0	11.26	8.8
H ₂	19.25	13.38	11.13	7.74	52.37
CH ₄	2.55	1.8	1.5	1.1	0.2
Energy parameters					
LHV [kJ/Nm ³]	4,466	3,680	3,446	3,396	9,671
Cold Gas Efficiency (%)	77	73	71	71	>95%

When char is gasified with pure steam, at about 600 °C, the syngas is a stream with high concentration of carbon monoxide and hydrogen. That composition gives as producer gas with higher heating value in excess of 9,000 kJ/Nm³. The use of pure superheated steam as the gasification agent gives a high-quality gas either as energy carrier or as feedstock for the production of chemicals through Fisher-Tropsch synthesis. Another relevant feature of the syngas obtained from charcoal gasification (air or steam) would be the very low tar concentration, as expected from the proposed two-step energy conversion system.

The syngas obtained after gasification of MSW-char was then consumed in an internal combustion engine, for heat and power production. Data from the gasification of char produced at 450 C was applied for the energy analysis. Moisture and ash content in MSW-char were 3 and 18% respectively. The gas engine performance data was taken from CAT G3512 which delivers up to 1.0 MW electric power per unit.

With syngas, engine derating is about 57%. Therefore, each unit would deliver 430 kW of electric power. The total power plant was designed to consume up to 15,000 kg/h of syngas from the air-gasification of 9209 kg/h of MSW-char in five G3512 gas generator sets. As reported by the manufacturer, engine electric efficiency is 35.1%. After correcting for engine derating, the total electric power output of the plant is 2.382 MW. The total heat rejected by the plant in the exhaust gas was inferred as 2.694 MW (@ 529 °C). The heat rejected by the jacket water would amount 2,0 MW. A total of 8.6 MW would represent unrecovered energy losses. The combined heat and power efficiency of the plant, based on the higher heating value of the MSW-char, would be 15,5%. The syngas specific fuel consumption would be 6,3 kg/kW-h.

Considering 20% of char yield from the carbonization of MSW, the plant would consume 46 metric tons of energy recoverable waste per hour. From which, the carbonization plant would produce near 36.8 metric tons of pyrolysis gas and waste oil. These high value energy products should also be employed for heat and power generation thus increasing the total capacity of the plant (Kumar and Samadder, 2017)

CONCLUSION

This paper presented the preliminary results of a thermochemical equilibrium model developed to assess the gasification performance of chars derived from slow pyrolysis of MSW. The obtained producer gas would be absent of tarry compounds thus claiming a simple low-cost gas cleaning system prior to its utilization in any heat engine cycle. Carbonization of MSW would take place in any off-the-shelf hardware available in the market due to the low heating rate and maximum temperature requirements for the conversion plant. Likewise, the gasifier would be of a single stage and the technology would be selected mostly based on the charcoal particle size, rather than from its composition in addition to the conversion rate. Gasification of charcoal from MSW produces a gas with improved composition and heating value as compared to the parent feedstock. Steam gasification of charcoal derived from MSW would further improve gas quality. The combined heat and power efficiency of the plant, based on the higher heating value of the MSW-char, would be 15,5% after gasification of about 9 metric tons of high quality MSW-char.

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