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Torrefaction of unutilized biomass resources and characterization of torrefaction gasses

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Contents

1. INTRODUCTION.....	3
2. TORREFACTION PROCESS	3
3. FEEDSTOCK FOR TORREFACTION PROCESSES	4
4. TORREFACTION GAS COMPOSITION AND UTILIZATION.....	6
REFERENCES.....	11



1. INTRODUCTION

Torrefaction is a thermal pre-treatment process improving the fuel properties of biomass. Major improvements are the better grindability, less moisture uptake, higher C/O ratio, and as such a higher heating value. Other positive effects of torrefaction are better ignition and combustion properties and a more favourable size distribution after grinding operations. Torrefaction is a mild roasting process in an inert atmosphere, and temperatures are typically ranging between 200 and 300 °C (Tumuluru, 2011). The treatment results in de-volatilization, de-polymerization and carbonization of the biomass. The products are a uniform solid mass of dark colour (torrefied biomass) torrefaction gas that consists out of condensable and non-condensable fraction. The condensable gases consist mainly of water, organics and lipids while the non-condensable fraction consist mainly of carbon dioxide and carbon monoxide. Typically about 70% of the mass is retained as a solid product, while 30 % of the mass is converted into gases and condensate. The solid fraction retains 90% of the initial energy content. This is the reason why the heating value of torrefied biomass is about 15-20 % higher compared to untreated biomass. Torrefaction has been shown to decrease the energy used for grinding biomass into small particles by about 70%. The particles of torrefied biomass have a favourable particle size distribution and shape for combustion processes. During torrefaction the number of hydroxyl groups is reduced significantly and this results in a lower ability to bind water. As a consequence biomass loses its high affinity for water, and is turned into a material with hydrophobic characteristics. Torrefaction is a widely discussed topic in the biomass and bioenergy industry right now and several initiatives are investigating the opportunities and market for torrefied biomass as a fuel in existing coal based heat and power plants. Torrefied biomass has “coal like” properties and makes it therefore particularly suitable for firing in existing CHP plants.

Wood is by far the most used biomass feedstock for torrefaction applications but several studies have been made about the torrefaction of other unutilized biomass feedstocks i.e. agricultural fibers. Two international research projects the EU projects SECTOR and LogistEC have started in 2012 and they will study the torrefaction and densification processes of a wide range of biomass resources. The present report will review torrefaction processes of unutilized biomass resources and provide information about the properties and composition of torrefied biomass and torrefaction gas

2. TORREFACTION PROCESS

Torrefaction processes are usually characterized by the following parameters: Reaction temperature 200-300 °C, heating rate < 50 °C, residence time < 30 minutes, ambient pressure (some technologies used pressurized reactors) and flexible feedstock. The absence of oxygen in the reactor is important to prevent oxidation and ignition of the biomass (Tumuluru, 2011).

The reaction in a torrefaction reactor can be separated into different phases. Initially when the biomass is heated up, unbound water is removed from the biomass, comparable to a drying process. Further heating of biomass removes bound water through chemical reactions, mainly condensation reactions. Once the biomass has reached a temperature above 160 °C, the formation of carbon dioxide begins (Zanzi et al, 2002). Further heating to a temperature between 180 to 270 °C results in decomposition of hemicelluloses. At this stage, reactions are partly exothermic and result in the release of numerous gaseous products (Torrefaction gas) of low heating value. At temperature above 280 °C the process becomes completely exothermic, and the amount of gaseous products increases significantly (Zanzi et al., 2002). Hemicelluloses are most sensitive to



thermal decomposition but also cellulose and lignin are degraded at high torrefaction temperatures. The different reaction products of biomass torrefaction are summarized in Figure 1.

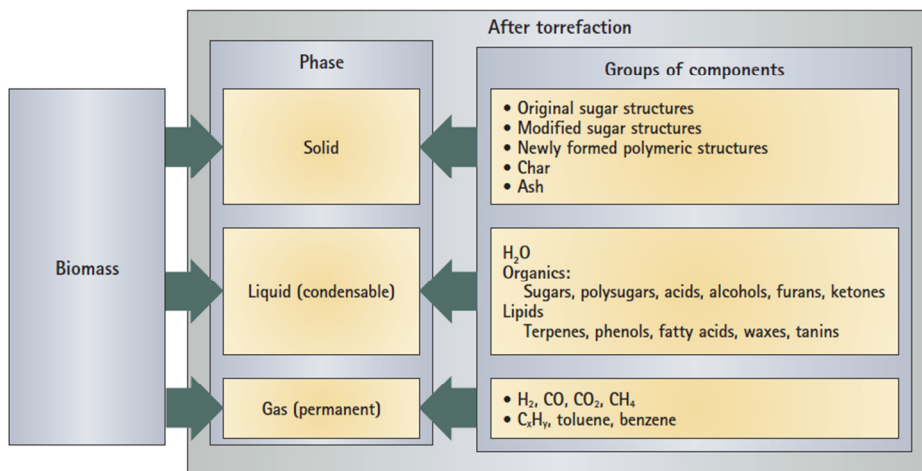


Figure 1. Products formed during biomass torrefaction (Figure from Tumuluru et al., 2011).

3. FEEDSTOCK FOR TORREFACTION PROCESSES

The global potential of biomass feedstock for torrefaction processes has recently been reviewed in a report by the international energy agency. Torrefaction is seen as a technology that broadens the feedstock base for bioenergy utilization beyond wood resources, especially when combined existing with densification technologies. Combined torrefaction and densification (i.e., pelletization) can increase the energy density of biomass by about five times. Combined torrefaction and densification also produce a biomass feedstock better suited for blending with coal, offering improved milling and handling characteristics and allowing the two to be blended prior to coal milling, which can potentially increase cofiring ratios (Tumuluru 2012).

An assessment conducted in Europe estimates total residue availability for torrefaction to be at about 4200 PJ (Deutmeyer et al., 2012)

Table 1 show the available biomass resources in the 27 EU countries and Table 2 shows the technical potential of biomass for energy in some selected Asian countries. Although the assessment of biomass resources is difficult and subject of vivid discussion it has to be noted that the data shows that there is a large unutilized potential especially in South East Asia, South America, Russia, North America and some parts of Europe.

**Table 1.** Residue Availability in Europe (PJ) (Deutmeyer et al., 2012)

	<u>Ag</u>	<u>Forest Processing</u>	<u>Logging Chips</u>	<u>Tree Chips</u>	<u>Roadside Hay</u>	<u>Construction</u>	<u>Total</u>
France	343.9	251.6	68.5	35.7	17.4	19.1	736.2
Germany	206.9	221.0	60.1	29.8	24.0	32.1	573.9
Sweden	24.3	256.8	69.9	41.5	2.6	0.1	395.2
Poland	165.7	127.8	24.6		11.3	15.0	344.4
Finland	20.1	211.7	57.6	36.0	1.5	3.0	329.9
Romania	146.4	52.0	4.2		6.5	8.7	217.8
Spain	141.5	36.7	10.0	13.9	11.9	2.7	216.7
UK	113.8	34.7	9.4	5.1	17.3	1.8	182.1
Other EU27	<u>491.1</u>	<u>456.4</u>	<u>120.6</u>	<u>43.3</u>	<u>51.6</u>	<u>41.9</u>	<u>1,204.7</u>
Total	1,653.7	1,648.7	424.9	205.3	144.1	124.4	4,200.9
Cost (€/GJ)	1.1–3.9	1.1–2.6	1.4–6.7	4.2–8.1	2.0	-4.6	

Table 2. Residue Technical Potential Asian Countries (TJ) (Deutmeyer et al., 2012)

	<u>Indonesia</u>	<u>Malaysia</u>	<u>Philippines</u>	<u>Thailand</u>
Forest residues	250	250	20	20
Agro-based wood residues	750	200	350	150
Field-based agro-residues	1,850	80	600	1,000
Agro processing residues	<u>600</u>	<u>150</u>	<u>300</u>	<u>450</u>
	3,450	680	1,270	1,620

Initial torrefaction studies focussed on the torrefaction of wood residues which comprise the largest available biomass resource. However wood resources are limited and therefore focus has been set on other unutilized biomass resources recently. Numerous studies have been made to test the torrefaction properties of agricultural fiber residues. Those biomass resources include wheat straw (Stelte et al, 2013), rice straw (Huang et al. 2012), palm fiber (Ke-Miao et al., 2012), rice husk (Wang et al., 2012; Chen et al., 2012), eucalyptus (Ke-Miao et al., 2012), pennisetum (Huang et al. 2012), sugar cane residues (Wang et al., 2012), corncobs (Zheng et al. 2012), cotton stalk (Patel et al., 2012) , prosopis (Patel et al., 2012) , sugar cane bagasse (Patel et al., 2012), coffee residue (Chen et al., 2012), corn stover (Medic et al., 2012), bamboo (Rousset et al., 2011), palm waste (Uemura et al., 2011), reed canary grass (Bridgeman et al., 2008).

Uemura et al. (2011) studied the torrefaction properties of oil palm waste. The palm oil industry is a multimillion dollar business and results in huge amounts of waste products such as empty fruit bunches (EFB), mesocarp fiber and kernel shell. There is limited use for those kind of residues at the present time and therefore they are an interesting feedstock for torrefaction processes. The residues are torrefied at different temperatures and change their chemical composition and physical properties as shown in Table 3 and Figure 2.



Figure 2. Images of Empty fruit bunches, mesocarp fiber and kernel shell after torrefaction at 220, 250 and 300 °C (Uemura et al, 2011).

During torrefaction the heating value is increased significantly and the chemical composition is altered due to a removal of volatile compounds during torrefaction (Table 1)

Table 1. Physical and chemical properties of torrefied oil palm residues after torrefaction (Uemura et al, 2011).

Biomass	Treatment	Calorific value (MJ/kg)			Elementary and ash analysis (wt.%)									
		HHV	LHV	Δ LHV	C	Δ C	H	Δ H	N	S	O	Δ O	Ash	Δ Ash
EFB	Dried	17.02	15.82	-	45.53	-	5.46	-	0.45	0.044	43.40	-	5.12	-
	Torrefied at 220 °C	17.17	16.14	0.32	46.75	1.22	4.68	-0.77	1.27	0.12	41.42	-1.98	5.75	0.63
	Torrefied at 250 °C	17.67	16.58	0.76	47.07	1.54	4.95	-0.51	1.35	0.11	42.24	-1.16	4.28	-0.84
	Torrefied at 300 °C	20.41	19.44	3.62	49.56	4.03	4.38	-1.08	1.27	0.02	43.19	-0.21	1.58	-3.54
Mesocarp fiber	Dried	19.61	18.31	-	46.92	-	5.89	-	1.12	0.09	42.66	-	3.32	-
	Torrefied at 220 °C	19.03	17.82	-0.49	46.93	0.01	5.50	-0.38	1.83	0.10	43.30	0.64	2.34	-0.98
	Torrefied at 250 °C	19.24	18.09	-0.22	47.70	0.77	5.20	-0.69	1.74	0.10	40.18	-2.48	5.10	1.78
	Torrefied at 300 °C	22.17	21.10	2.78	48.60	1.68	4.87	-1.02	2.14	0.09	40.03	-2.63	4.26	0.94
Kernel shell	Dried	19.78	18.49	-	46.68	-	5.86	-	1.01	0.06	42.01	-	4.38	-
	Torrefied at 220 °C	18.85	17.46	-1.03	45.87	-0.81	6.31	0.45	0.40	0.02	43.07	1.06	4.33	-0.05
	Torrefied at 250 °C	19.07	17.82	-0.67	51.89	5.20	5.71	-0.15	0.47	0.01	38.50	-3.51	3.42	-0.96
	Torrefied at 300 °C	21.68	20.56	2.07	54.21	7.52	5.08	-0.78	0.50	0.02	36.66	-5.35	3.53	-0.85

4. TORREFACTION GAS COMPOSITION AND UTILIZATION

The heating of biomass during torrefaction results in the release of gaseous products from biomass. The major components of torrefaction gas are water and CO₂. However it contains also a variety of combustible organic compounds. The amount of torrefaction gas released from the biomass depends on heating rate, temperature, reaction time and biomass composition. The water content in the torrefaction gas depends on feed stock moisture content. Even totally dry biomass results in a water content of about 50% (wt) in the torrefaction gas and 10% (wt) CO₂ due to chemical reactions (Tumuluru 2010). The total amount of incombustible gases in torrefaction gas is therefore at about 60% (wt).

Bergman (2005) and Bergman et al. (2005) have investigated the composition of torrefaction gas in great detail. Water comprises for about 5 to 15% (wt) of the total yield of the torrefaction process which is 50 to 80% (wt) of the torrefaction gas (excl. free water from feedstock). The absolute amount of water increases with reaction time and temperature, while its relative amount, in relation to other torrefaction gas components decreases. The amount of combustible gases increases with temperature and reaction time. The calorific



value of torrefaction gas has been determined to be in the range of about 5.3 to 16.2 MJ/Nm³. Tumuluru et al. (2010) compared the heating value of torrefaction gas with producer gas from thermal gasification of biomass (4 to 5 MJ/Nm³) and syngas in indirectly heated gasification processes (15 to 20 MJ/Nm³). The comparison shows that torrefaction gas is suitable for combustion and most torrefaction processes (process scenarios) use the heat obtained from its combustion in the process itself i.e. for biomass drying.

However there might be alternative uses for torrefaction gas, especially the condensable fraction.

Condensable gasses

The condensable fraction of torrefaction gas consists mainly of water, acetic acid, aldehydes, alcohols, ketons and a wide range of lipids such as terpenes, phenols, fatty acids, waxes etc. (Figure 3).

According to Tumuluru et al. (2011) the condensable components can be subdivided into four groups:

- Freely bound water released through evaporation
- Reaction water (from thermal decomposition)
- Liquid organic compounds i.e. alcohols, organic acids, aldehydes, ketones etc.
- Lipids i.e. waxes and fatty acids

Water is the major condensable product of biomass torrefaction processes. It is either from the evaporation of freely bound water or a reaction product of chemical dehydration and condensation reactions. Other condensation products are acetic acid, formic acid and methanol, originating from the side chains and substituents of the hemicellulose. Furthermore lactic acid, furfural, hydroxyacetone and phenol can be found in the condensate fraction. Their quantity in the torrefaction gas depends mainly on the torrefaction temperatures as shown in Figure 4.

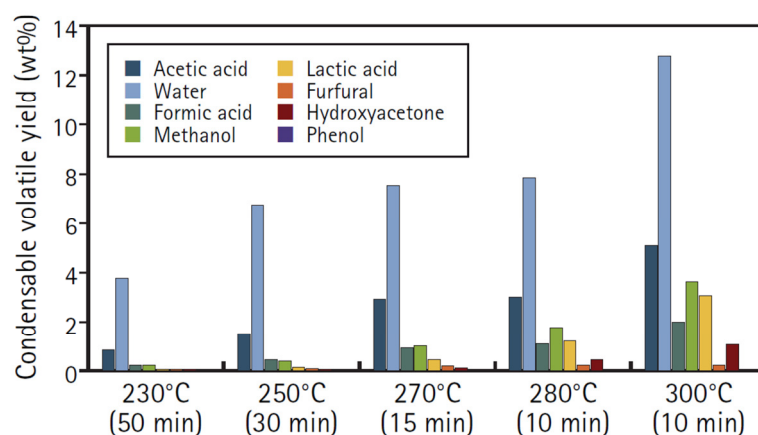


Figure 3. Yield of condensable during biomass torrefaction (Tumuluru et al, 2011).

The composition of the condensable volatiles is also depending on the feedstock, as shown in Figure 3. The differences are mainly based on volatile content and substituents of the lignin and hemicelluloses, of the original feedstock.

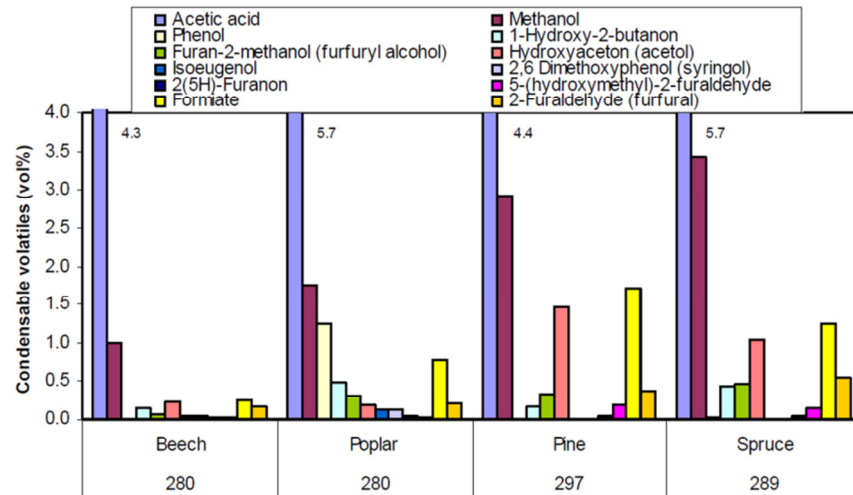


Figure 4. Yield of condensable volatiles for different wood species (Verhoeff et al., 2011)

The differences between feedstock become even more prominent when comparing wood type feedstock (Figure 4) with agricultural grasses as shown in Figure 5.

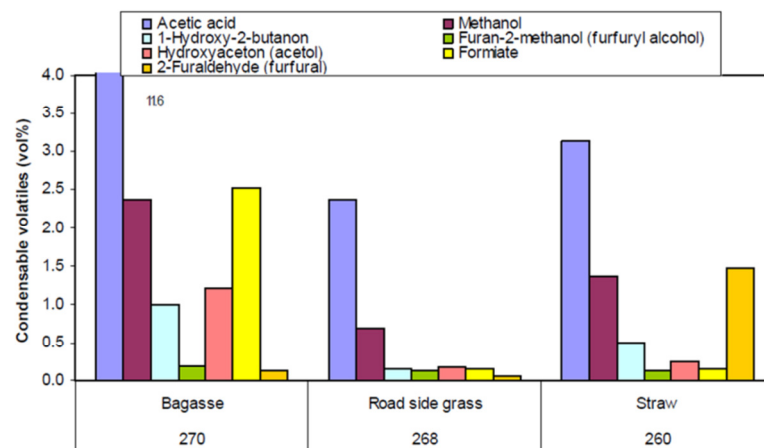


Figure 5. Condensable volatiles released during the torrefaction of agricultural grasses (Verhoeff et al., 2011).

The composition of the condensable fraction from the torrefaction of waste products, refuse derived fuel (RDF) and Trockenstabilat is shown in Figure 6. They consist mainly of combustible components of municipal waste such as plastics and biodegradable waste. The presence of petrochemicals in municipal waste might be the reason for the different composition, compared to torrefaction gas derived from wood and grass.

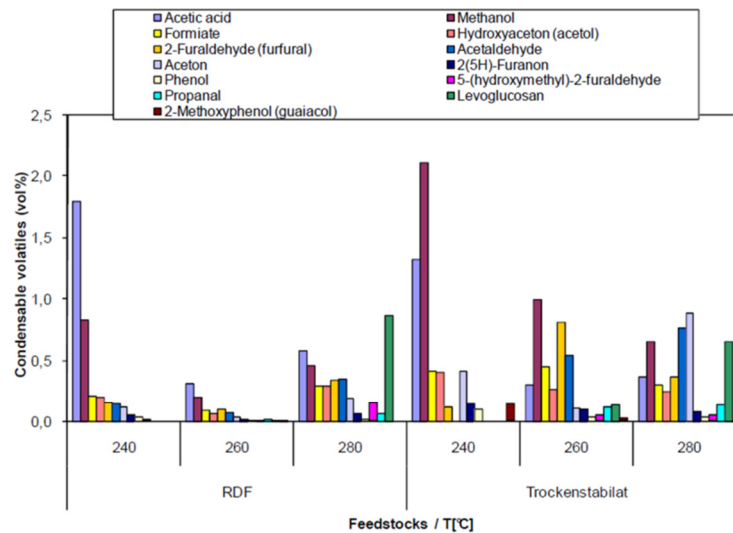


Figure 6. Condensable volatiles released during the torrefaction of organic waste streams (Verhoeff et al., 2011).

From Figures 3 to 6 it can be concluded that the major condensable compounds, for all feedstock and torrefaction temperatures, are acetic acid, methanol and formic acid.

Non-condensable gasses

The majority of non-condensable gasses formed under torrefaction are carbon dioxide (CO₂) and carbon monoxide (CO). CO₂ is formed due to decarboxylation and dehydration reactions while CO is most likely a reaction product of CO₂ and steam with char (White and Dietenberger, 2005). There are traces of hydrogen and methane in the torrefaction gas but their concentrations are so low that they can be neglected as potential side streams. The release of CO and CO₂ depends on the temperature and feedstock. An example for larch, torrefied between 230 and 290 °C compared to wheat straw, torrefied at 250 °C, is shown in Figure 7.

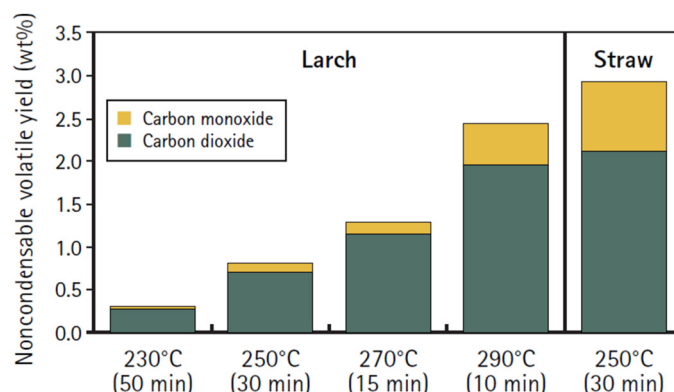


Figure 7. Non-condensable torrefaction gasses released at temperatures between 230 and 290 °C (Tumuluru et al, 2011).



Torrefaction gas is a mixture of different components, and is usually combusted on production site, to use the heat within the torrefaction process or biomass drying. Apart from incineration, torrefaction gas might be used for the production of green chemicals. From the condensable fraction of torrefaction gas, chemicals, such as concentrated acetic acid, formic acid, methanol and furfural could be produced. The yield depends on feedstock and torrefaction parameters (Figures 3 to 6).

Acetic acid: Acetic acid is the major condensable product that can be obtained from torrefaction gas. Its concentration can be up to 5 % (Vol.) of the gas fraction. The major use of acetic acid is for the production of vinyl acetate monomer (VAM), which is polymerized to polyvinyl acetate (PVA). PVA is widely used as an adhesive for porous materials, i.e. wood and paper. Alternative uses can be for ester production (i.e. ethyl acetate) that is mainly used as solvent for inks, paints and coatings, or the production of acetic anhydride which is mainly used as acetylation agent in the production of acetylated specialty chemicals, i.e. cellulose acetate.

Formic acid: Formic acid is the simplest carboxylic acid. It is an important intermediate in chemical synthesis, i.e. the production of pharmaceuticals, such as antibiotics, sweeteners, plasticizers, plant protection agents and antioxidants. Formic acid is also used in the production of leather, and for dyeing and finishing of textiles. Other applications are cleaning products, preserving agents or as antibacterial agent in livestock.

Furfural and its derivatives are used in the chemical industry. Furfural is an important renewable, non-petroleum based, chemical feedstock. Furfural is used as a solvent and for the production of furfuryl alcohol (FA). FA is further hydrogenated to tetrahydrofurfuryl alcohol (THFA) and tetrahydrofuran (TFH). TFH is used for the production of specialty chemicals while THFA is used as solvent and adjuvant in plant pesticides.

Methanol, also known as wood alcohol is a common laboratory solvent, especially used in chromatography and analytical chemistry. Methanol is used as a precursor for the production of other chemicals. Its first converted into formaldehyde and then used for the production of plastics, plywood, paints, explosives, and permanent press textiles. Alternative uses are as fuel in vehicles, antifreeze agent or denaturizing agent.

Most other condensable compounds from torrefaction gas could theoretically be used in the chemical industry either a precursor for other products or as solvents. However in most cases a high purity is required and there are alternative established production processes that are more reliable and cost efficient. Liquid condensable are a mixture of chemicals and need to be separated and purified before they can be used. The torrefaction condensate as such could be used for coating of pellets produced from torrefied biomass to increase the hydrophobicity of the biomass. Also the use of condensate as additive in pelletizing processes has been discussed since it contains waxes and fatty acids that might decrease the friction during processing. Further studies are required to evaluate the potential of the condensable fraction from torrefaction gas. Looking at the non-condensable gases (CO and CO₂) they may be used as inerting agent to prevent oxidation and ignition of the biomass in the process.



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