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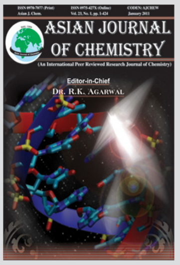

Production of Liquid Fuels from Vacuum Pyrolysis of Chinese Bicycle Tire Wastes

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This study is based upon fixed bed reactor under vacuum conditions by applying Chinese bicycle tire wastes as the pyrolysis feedstock. The influence of temperature on this process was investigated. It has been found that 450 ºC is the optimum temperature, at which the yield of pyrolytic oil is 45.2 wt %. The raw materials were characterized by elemental analysis and thermal gravimetric analysis, from which the major composition of bicycle tire wastes can be obtained. Pyrolytic oils were characterized by elementary analyses, FT-IR and GC-MS. These results show that the pyrolytic oil has high heat value of 41-43 MJ/kg, which can be used as potential liquid fuel after proper modification and also can extract some valueable chemical products.

Key Words: Vacuum, Pyrolysis, Bicycle tire wastes, Fixed bed reactor, Pyrolytic oils.

INTRODUCTION

It is known that China has a population of 1.3 billion among which about 400 million people are using bicycles. According to China's National Bureau of Statistics, about 150 million tires became solid wastes in 2008 and were waiting for disposal and this number is still increasing. The disposal of waste tires has been proved to be greatly difficult because of their highly resistant chemical, biological and physical properties[1]. Most of the scrap tires generated are dumped in open or landfill sites[2]. Which will not be degradated in natural state for decades. Therefore, a lot of environmental issue have been arise, such as deteriorating soil quality, occupying a lot of space and catching fire easily, even causing potential health problem to human beings. In order to avoid these problems and economically make use of wasted tires, some methods using for recycling have been reported. Basically, three broad categories of scrap tire rubber have been considered such as chipped, crumbed and grounded rubber, depending on the type of size reduction equipment and intended applications[3,4]. Usually, tire reprocessed into recovered rubber, such as tire retreading, athletic surfaces, playground surfaces, as well as civil engineering applications, such as retaining walls, void filler, *etc*. These disposal are currently the main markets for waste tires[5].

From recent literatures, wasted tires can also be used for thermal energy applications. Tires are mainly constituted by natural rubber (NR), styrene butadiene rubber (SBR), butadiene rubber (BR), carbon black and other tire additives which have high volatile and fixed carbon and the calorific value of waste tires is high, around 28-37 MJ/kg[6]. The main components above with a high heating value that considered as a feasible alternative for energy recover[7].

It is well known that waste tires is characterized as high-volatile and low-ash contents and has higher heating value than coal and biomass. These characteristics make it an ideal material for combustion, pyrolysis and gasification[8]. Among the thermal destruction technologies, the pyrolysis process seems to be more attractive in comparison with the other treatments in terms of minor environmental crash[9]. Pyrolysis generally decomposes the waste tire at high temperatures of 300-900 ºC in the inert atmosphere. Three major phases obtained from pyrolysis of waste tire are high energy liquid, gas and solid char. Rodriguez *et al.*[10], reported that tire-pyrolytic liquid are a complex mixture of C_5-C_{20} organic compounds, with a great proportion of aromatics and also have a high gross calorific values of around 41-44 MJ/kg. Similar results were also found by Cunliffe *et al.*[11], as they reported that major pyrolytic oil components are light aromatics such as benzene, toluene, xylene (BTX) and limonene *etc*., which command a higher market value than the raw oils. According to those reports, pyrolytic oils can be used for fuels directly or extracted high value chemical raw material. At the same time, gases are useful as fuel or chemical raw material. Also, solid char may be used either as smokeless fuel, carbon black or activated carbon or can be gasified for production of fuel gases[12].

In order to increase the yield of pyrolytic oil, some researchers used various gases as carrier gas to remove the pyrolytic products from reactor rapidly. The secondary reactions can also be decreased and sulfur can be removed. Mastral *et al.*[13], reported that two different batch reaction systems and a continuous reactor were tested under hydrogen pressure (ranging from 1-10 MP). They drew the conclusions that hydrogen pressure did not significantly affect tire conversion, always achieving the maximum possible conversion, independently of the reactor type. Islam *et al.*[14], demonstrated the pyrolysis behaviours of the wasted bicycle/rickshaw tire including pyrolytic product yields and product characteristics. They also reported that bicycle/rickshaw tire wastes available in Bangladesh were pyrolyzed in a fixed-bed fire-tube heating reactor under different pyrolysis conditions to determine the role of final temperature, sweeping gas flow rate and feed size on the product yields and liquid product composition.

Vacuum pyrolysis was used for decomposing waste tires under vacuum conditions with a total pressure lower than 10 kPa and relative temperature. Roy *et al.*[15], have done a series of studies on vacuum pyrolysis of waste tires and biomass. They reported that the oil yield (43-47 wt. %) with the vacuum process was higher than the oil yield from an atmospheric pyrolytic process. These differences can be explained by the different residence time of the pyrolytic products in the reactor in the atmospheric and vacuum pyrolytic reactors. In the vacuum process, the pyrolytic products are rapidly removed from the reactor by the vacuum pump. Thus, the residence time of the pyrolytic products inside the reactor is relatively short and secondary reactions involving the primary fragments are limited. Similar results were also conducted by Zhang *et al.*[16], they reported that the pressure of pyrolytic system was maintained at 3.5-4.0 kPa. At a temperature of 450 ºC, the yield of oil was rather low and residue was about 50 wt %.

In this paper, a type of Chinese bicycle tire rubber was chosen as the feedstock. The samples of bicycle tire rubber were characterized by elementary analysis and thermo-gravimetric analysis. Major component of bicycle tire and optimal pyrolytic temperature were analyzed. Pyrolysis runs were performed at different temperatures (400-500 ºC) under vacuum conditions (4-6 kPa). The light and heavy fraction of the pyrolytic oils obtained from vacuum distillation. According to GC-MS analyses, the content of limonene increased in the light fraction in this paper.

EXPERIMENTAL

The bicycle tire wastes have been taken into consideration as materials throughout the experimental studies, which were collected locally from Nanjing city garage. Bicycle tire granules were used for all of the vacuum pyrolysis runs, which were sieved to a size range of 5 mm × 8 mm-10 mm × 15 mm (cross-section).

Experimental apparatus and process of vacuum pyrolysis: Bicycle tire granules were performed in a stainless steel fixed bed reactor with an inner diameter of 219 mm and a height of 460 mm. A schematic diagram of the experimental apparatus of vacuum pyrolysis is shown in Fig. 1. In this process, bicycle tire granules were fed under vacuum into reactor. The system was evacuated rapidly by a vacuum pump which maintained a total pressure of 4-6 kPa (absolute). The reactor was heated directly by a tubular furnace maintained a temperature of 400-500 ºC at an average heating rate of 20 ºC/min and a thermocouple inserted into the reactor was measured the internal temperature. During the vacuum pyrolysis, the vapors were extracted from the reactor and cooled down by condensation system which maintained at 0, -20 and -40 ºC, respectively. The non-condensed gases were pumped out to a gas storage cylinder. The solid residues in the reactor were char, which can be used as carbon black. The absorbing bottle was used not only for absorbing NO_x, SO_2 and H_2S in the non-condensed gases, but also for controlling the pressure of the vacuum pyrolysis unit.

Stop heating system and the vacuum pump when the process of vacuum pyrolysis completed. The reactor was swept by the nitrogen that can avoid any oxidation of pyrolytic products and cool down the reactor. The weight of liquid and solid residues was measured.

Analysis: Elementary analysis of the bicycle tire granules and pyrolytic oil were performed by Elementar vario EL III. The higher heating value (HHV) was calculated based on the Dulong formula[17]: $\text{HHV (MJ/kg)} = 0.3383 \times C + 1.442 \times (H - O/8)$. In which, C, H and O represent the weight percentages of carbon, hydrogen and oxygen, respectively.

SDT-Q600 thermo-gravimetric analyzer was applied for the thermo-gravimetric tests. The samples were heated from 30-600 ºC under a nitrogen flow at 10 and 20 ºC/min, respectively. The bicycle tire was milled and screened to 1 mm for the samples of *ca.* 20 mg which were used for the thermo-gravimetric tests. FT-IR (Spectrometers-750, Nicolet, USA) was used for analyzing light and heavy fraction of pyrolytic oil.

GC-MS analysis: The analysis of pyrolysis oil was performed on GC system (GC 7890A) equipped with a FID

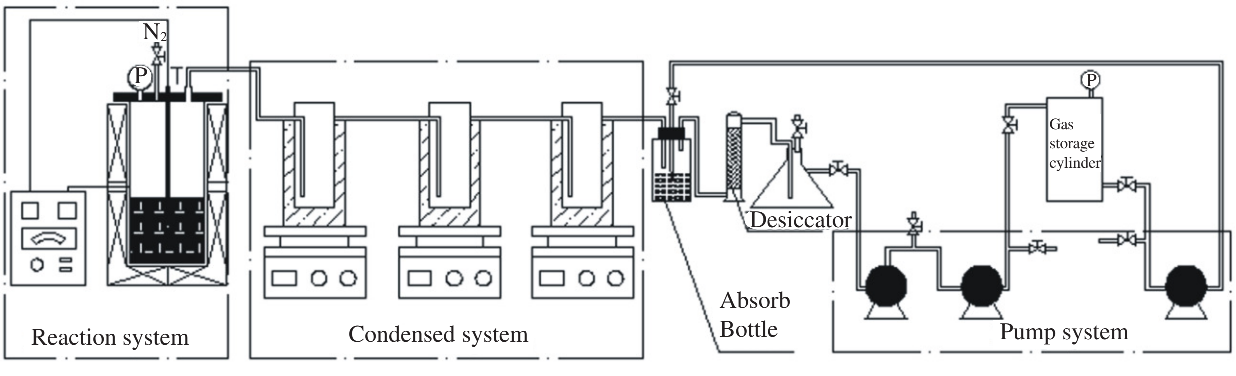

Fig. 1. A schematic diagram of the experimental apparatus of vacuum pyrolysis

and DB-5 column. The GC oven temperature was held at 100 ºC for 2 min and then programmed to 300 ºC at 10 ºC/min^{-1}. The injector temperature was 300 ºC with split mode. FID was maintained at 300 ºC. Nitrogen was the carrier gas. The mass spectrometer operating conditions were: transfer line 250 ºC, ion source 230 ºC, electron energy 70 eV.

RESULTS AND DISCUSSION

Major composition of bicycle tire and reaction temperature: The elemental composition and higher heating value (HHV) of the tire granules are shown in Table-1. The higher heating value (HHV) was calculated based on the Dulong formula. The bicycle tire material used in this work was a rubber free of steel. It is axiomatic that the major components of tires are nature rubber (NR), styrene butadiene rubber (SBR) and butadiene rubber (BR). The structure of NR, SBR and BR is shown in Fig. 2. The tires mostly consist of two or three rubbers together.

TABLE-1
ELEMENTAL COMPOSITION AND HIGHER HEATING VALUE OF FEEDSTOCK

Elemental composition (wt. %)	Present study (bicyle tire)
Carbon	75.30
Hydrogen	7.60
C/H (mol/mol)	0.83
Nitrogen	0.80
Sulfur	1.53
Oxygen*	14.77
HHV (MJ/kg)	35.77

*Calculated by difference (include: oxygen + ash).

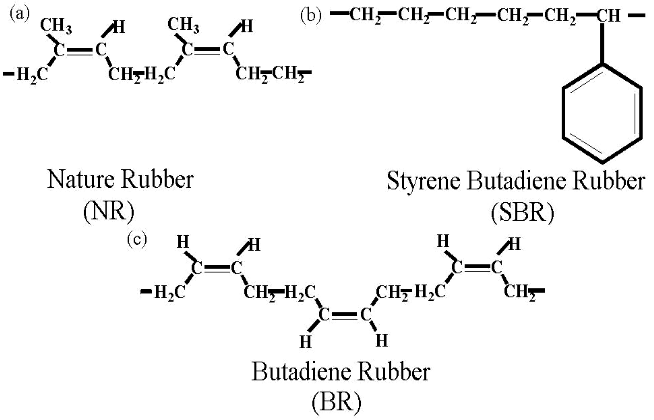

Fig. 2. Structure of natural rubber (a), styrene butadine rubber (b) and butadiene rubber (c)

A typical sample of the bicycle tires had been prepared for thermogravimetric analysis. The tire samples (about 20 mg) were heated over the temperature range of 30-600 ºC at constant heating rates of 10 and 20 ºC/min in a high purity nitrogen atmosphere with a flow rate of 150 mL/min. Thermogravimetric analysis was used to achieve the optimum pyrolytic temperature and analyze the major composition of bicycle tire wastes. Meanwhile, thermogravimetric analysis and differential thermogravimetric plots for bicycle tire wastes at heating rates of 10 and 20 ºC/min were shown in Fig. 3.

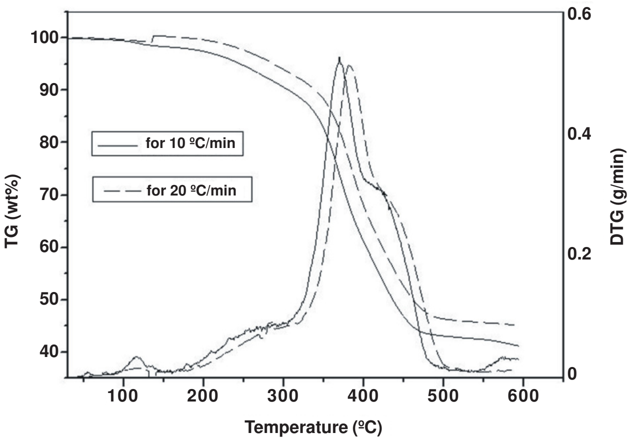

Fig. 3. TG and DTG plots for bicycle tire wastes at heating rates of 10 and 20 ºC/min

Some researchers proposed that the thermal degradation behaviour of waste tires gives information about the own characters of rubber. Williams *et al.*[18], reported that during thermal decomposition, natural rubber (NR) gives a sharp peak at 375 ºC, styrene butadiene rubber (SBR) gives comparatively a round peak at around 450 ºC, whereas butadiene rubber (BR) gives two peaks at 400 and 475 ºC for a heating rate of 5 ºC/min. Seidelt *et al.*[19], investigated DTG curves of three different rubbers NR, SBR and BR and reported that DTG curves can be characterized by their peak temperature: 378 ºC for NR, 430-458 ºC for SBR and 468 ºC for BR. In their studies, they found very sharp peaks for NR and BR at the specified temperatures and a round peak for SBR, which started at about 430 ºC. Therefore, it can be concluded that when the composition of tires contains NR, SBR and BR, a sharp peak at around 370 ºC, a round peak after 400-460 ºC and another sharp peak at around 460 ºC must be found in their DTG curve, respectively.

The DTG curve obtained at heating rates of 10 ºC/min for the representative samples of bicycle tire waste is presented in Fig. 3. There are two processes of maximum weight loss. The first sharp peak at 374 ºC can demonstrate that bicycle tire rubber contains NR. A slight round peak over a temperature range of 430-455 ºC in the DTG curve for heating rate of 10 ºC/min indicates the trace amount of SBR.

Fig. 3 shows three steps of weight loss of bicycle tire wastes. The first step between 150 and 350 ºC is caused by a small amount of water, the volatilization of processing additives, mainly oils and plastizisers. The second step between 350 and 410 ºC can be attributed to the decomposition of NR. The third step between 410 and 500 ºC is caused by SBR.

In conclusion, major components of the representative sample of Chinese bicycle tire rubber are NR and SBR. A round of 450 ºC is the perfect temperature of pyrolysis, which can obtain the higher yield of products.

Vacuum pyrolytic product yields: The yields of liquid, char and gas obtained from vacuum pyrolysis of prepared sample for the temperature range of 400-500 ºC at every 50 ºC are listed in Fig. 4. The total pressure of pyrolysis system was maintained at 4-6 kPa. Fig. 4 shows that when the pyrolysis temperature increases from 400-500 ºC, the yield of liquid increases first from 38.5 ± 2.7 wt % to a maximum value of

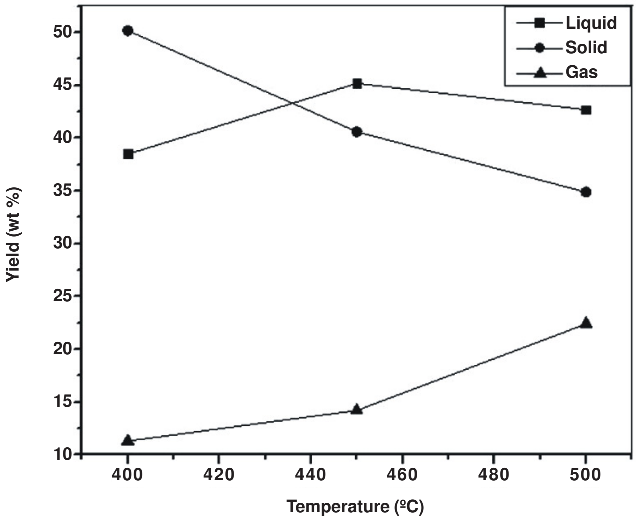

Fig. 4. Yields of products under different vacuum pyrolytic temperature

45.2 ± 1.5 wt % at 450 ºC and then decreases to 42.7 ± 1.9 wt %. The char yield decreased from 50.2 ± 3.1 wt % to 34.9 ± 2.5 wt % over the total temperature range, while gas yield increased from 11.3 ± 0.5 wt % to 22.4 ± 1.2 wt %. Tire pieces are not pyrolyzed completely at a temperature less than 450 ºC.

The yields of vacuum pyrolytic product and their distributions over the whole range of temperature depend not only on the bicycle tire composition, reaction temperature and vacuum pressure used for the experiments; but also on the size of bicycle tire, reaction residence time, the efficiency of condensation system, the distinguishing feature of the reaction system used, such as size and type of reactor and efficiency of heat transfer from the hot reactor surface to bicycle tire mass, *etc*.

Composition of pyrolytic oils

Elemental analysis for pyrolytic oils: The pyrolytic oil obtained from vacuum pyrolysis of bicycle tire wastes presents dark colour with strong and terrible smell. Results of elemental analysis of pyrolytic oil derived from different pyrolysis temperature are shown in Table-2. The physical and chemical properties of pyrolytic oil vary with pyrolysis temperature. According to the Dulong formula[17], the higher heating value calculated is also shown in Table-2. It is already known that higher heating value (HHV) of pyrolytic oil is 42.73 MJ/kg in the reaction temperature of 400 ºC, 42.09 MJ/kg in the reaction temperature of 450 ºC and 41.39 MJ/kg in the reaction temperature of 500 ºC, respectively.

TABLE-2
ELEMENTAL ANALYSIS OF PYROLYTIC OIL

Entemental content (wt. %)	400 (ºC)	450 (ºC)	500 (ºC)
Carbon	83.91	84.43	84.54
Hydrogen	10.38	9.82	9.50
C/H (mol/mol)	0.67	0.72	0.74
Nitrogen	0.99	1.03	1.05
Sulfur	0.52	0.58	0.63
Oxygen*	4.20	4.14	4.28
HHV (MJ/kg)	42.60	41.98	41.53

*Calculated by difference.

FT-IR analysis for pyrolytic oils: Pyrolytic oils are the major products of vacuum pyrolysis of bicycle tires waste. Since these oils consist of numerous components, which are difficult to seperate. Light fraction and heavy fraction of pyrolytic oil were obtained by vacuum distillation under the vacuum pressure of 4 kPa and temperature of 80 ºC and analyzed by FT-IR which was shown in Fig. 5.

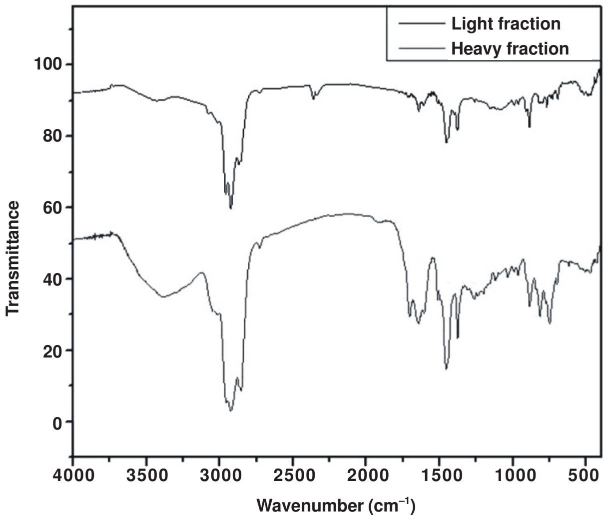

Fig. 5. FT-IR of light and heavy component

Compared with the results of Islam *et al.*[14], Gonzalez *et al.*[20] and Williams *et al.*[21] and from Fig. 5, the C-H stretching vibrations at 3000-2800 cm^{-1} and C-H deformation stretching vibrations at 1365-1470 cm^{-1} indicate the presence of alkanes. The C=O stretching vibrations at 1750-1650 cm^{-1} indicate the presence of aldehydes or ketones. The C=C stretching vibrations at 1685-1635 cm^{-1} indicate the presence of alkenes. The peaks between 890-685 cm^{-1} represent C-H out-of-plane bending, indicating the aromatic compounds. Comparing light fraction with heavy fraction in Fig. 5, heavy fraction has some obvious stretching vibrational absorption at 3400-3300 cm^{-1} representing O-H stretching, which are indicating of alcohols, phenols and carboxylic acids. And the C-N stretching vibrations at 1360-1250 and 1200-1025 cm^{-1} indicate the presence of amine, the S-O stretching vibrations at 1000-750 cm^{-1} indicate the presence of sulphide.

GC-MS analysis for pyrolytic oils: The pyrolytic oils derived from waste tires pyrolysis were complex mixture. GC/MS analyses were performed on the light and heavy fraction of the pyrolytic oils obtained from vacuum distillation under the vacuum pressure of 4 kPa and temperature of 80 ºC. Fig. 6 shows the light and heavy fraction of total ionization chromatography (TIC) figure and peak identification was performed using National Institute of Standards and Technology (NIST) workstation. It can be seen that the heavy fraction contained large amounts of benzene derivatives, limonene and other cycloalkenes, in comparison, the light fraction contained six major component. Pakdel *et al.*[22], reported that limonene can be used as an industrial solvent, a dispersant for pigments and a feedstock for the production of fragrances and flavorings. According to GC-MS analyses, the content of limonene is 8.94 wt % in the heavy fraction that is less than 23.17 wt % in the

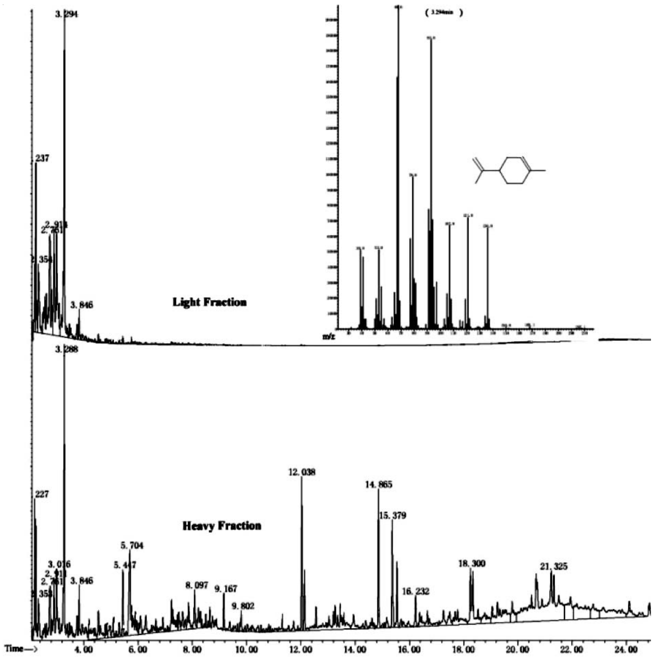

Fig. 6. Light and heavy component of TIC

light fraction. Because the limonene has high economic value and extensive applications, the light fraction can be used as important chemical industrial product.

Conclusion

Analysis of experimental data show the mass fraction and HHV of bicycle tire are 75.30 wt % and 35.77 MJ/kg, respectively. Major components of the representative sample are natural rubber and styrene butadiene rubber and the ideal pyrolytic temperature of bicycle tire is around of 450 ºC, which can obtain the higher yield of pyrolytic oils. The heavy fraction of pyrolytic oils contained large amounts of benzene derivatives, limonene and other cycloalkenes that can be used not only as fuel, but also as chemical industrial product. The content of limonene is 23.17 wt % in the light fraction.

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