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Computational Study on Kinetics of Conversion of Bio-oil Model Compound – Anisole, to Platform Chemicals

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Abstract. With the rise in the need of clean and renewable energy source, lignocellulosic biomass has gained significant attention across the globe. The major reason for its use as a fuel is the compatibility of biomass derived bio-oil with the conventional energy infrastructure. But the derived bio-oil contains over 300-400 components, most of which are not viable to be used as fuel due to the presence of oxy groups which decrease the energy density of the fuel. Thus, the bio-oil needs to be deoxygenated in order to increase its calorific value. In this study, anisole is taken as a model component representing phenolic fraction of the bio-oil. First, a bond dissociation energy (BDE) calculation is performed on optimized anisole structure to understand the energy requirement of breakage of bonds present in it. Consequently, three different pathways are proposed to convert anisole to benzene, phenol and toluene. Since the reaction is occurring in aqueous phase, direct hydrogenation of anisole is also proposed in an additional pathway. The proposed pathways are studied under the density functional theory (DFT) framework using B3LYP functionals with 6-311+g(d,p) basis set in aqueous phase with SMD solvation model. Finally, the thermochemical parameters are calculated for 298 K to 698 K temperature range. It is observed that the anisole can be reduced to benzene with lowest energy requirement among the proposed pathways. In general, increase in temperature cause decrease in Gibb's free energy change and enthalpy change of the reactions, thereby increasing reaction favourability.

1. Introduction

The demand for clean and sustainable energy has risen quite steadily over the last 20 years. The growing energy demand [1], depleting reserves of fossil fuel [2] and environmental concerns [3] has led researchers to investigate alternative sources of energy throughout the world. As a result, several clean energy technology like wind energy, solar energy, geothermal energy, biomass energy, etc. have emerged as potential substitute to conventional sources. Of all these, biomass is the only alternative capable of providing carbon based sustainable fuel which can be used directly as a replacement to petroleum energy [4]. Biomass energy can be utilized in the form of bio-oil which is obtained by thermochemical treatment of biomass [5]. Thermochemical treatment, like liquefaction and pyrolysis, directly converts the biomass into bio-oil [6]. However, this bio-oil contains several oxy-functional compounds. The presence of oxygen deteriorates the quality of the fuel causing low pH, low pour point, high viscosity, low stability and low energy density [4,7–9]. Thus, it is desired to eliminate the oxy functionals from the bio-oil to make it sufficiently viable as conventional fuel substitute. One of the most widely used technique to upgrade bio-oil is the hydrodeoxygenation (HDO) process.

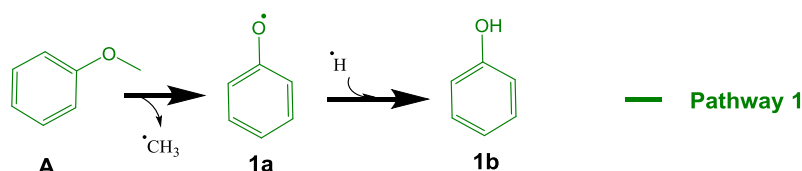


HDO of bio-oil has been studied by many researchers world over. Owing to a large number of compounds in the bio-oil, generally a model compound like guaiacol [10–12], phenol [13,14], ferulic acid [15,16], is selected as representative of the bio-oil for study. The presence of methoxy group in anisole makes it fairly representative of the phenolic fraction of bio-oil. Thus, it has been considered as the model compound for several studies. In a study conducted by Pizarro et al. [17], HDO of anisole has been conducted with Ni and Co catalyst with different zeolite bases. Among different product compounds like cyclohexane and cyclohexanol, they report the formation of phenol and benzene in the product mixture. In another study conducted by Parmon et al. [18], the anisole has been upgraded by HDO using Ru, Ni and Ni-Cu based catalysts at 300 °C and 1 MPa pressure. They found the Ni-Cu catalyst to give 100% HDO conversion over CeO₂ support with a selectivity of over 70% for alkanes. They also report that Ni over Al₂O₃ catalyst provide over 95% HDO conversion of anisole at same conditions. Resasco et al. [19] studied the effect of bifunctional catalyst using Pt doping over H-β zeolite. They studied the effect of aqueous medium on the rate of reaction and report a significant drop in anisole conversion in the absence of water. Similar findings are reported by Resasco et al. again in another work [20] where they studied the effect of water on HDO of anisole over HZSM-5 catalyst at 400 °C. In this study, the anisole conversion increased by 2.5 times in aqueous phase when compared to non-aqueous phase reaction and phenol yield reached over 35% at 70% anisole conversion. Gu et al. [21] have also reported the conversion of anisole to different end products like cresol, toluene and xylene, computationally using DFT. They state that the use of catalyst reduce the activation energy by 40 to 60 kcal/mol when compared with non-catalytic gas phase reaction. In another study [22], the pathway for decomposition of anisole has been studied experimentally and computationally by Sautet et al. who report the energy for the formation of phenol to be 22.23 kcal/mol and for the formation of benzene to be 19.35 kcal/mol over Pt (111) catalyst surface. The lower energy barrier for benzene formation has been ascertained as the cause for the high selectivity of benzene over phenol formation in the product composition.

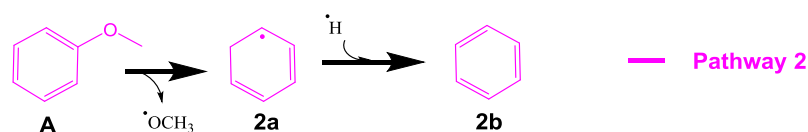
The bio-oil upgrading has been studied by many researchers using different catalytic and non-catalytic systems, both - experimentally and computationally. All the experimental study show that the presence of water shifts the reaction kinetics in favorable direction. However, as per the author's knowledge, there has not been much study on the kinetics of HDO of bio-oil in aqueous medium for non-catalytic system. Thus, in this study, the kinetics of HDO of bio-oil is determined using anisole as model compound in the aqueous phase under the density functional theory framework.

2. Reaction Scheme

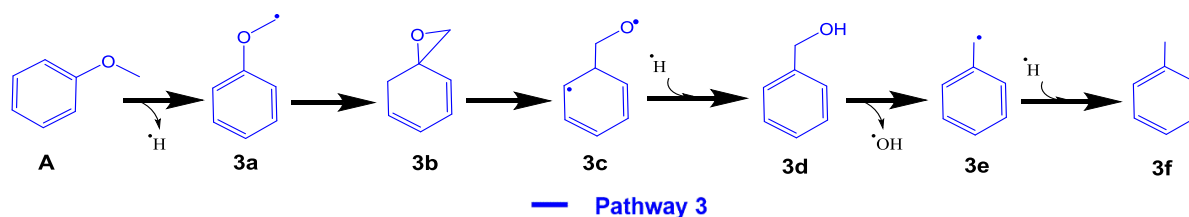
Anisole is proposed to be converted into phenol, benzene and toluene based on its bond dissociation energy (BDE) analysis via 3 different pathways- pathway 1, pathway 2 and pathway 3. Due to the presence of water as reaction medium, [•]H radicals present in the system are mobile enough to attack at the initiation of reaction. Thus a 4th pathways is also proposed describing direct hydrogenation of anisole.



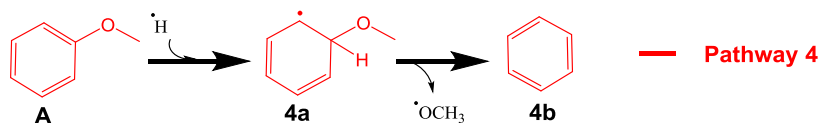
Pathway 1 initiates with the cleavage of the methyl group from the anisole to produce structure **1a**. The structure **1a** is then protonated to produce structure **1b** (phenol).



In pathway 2, the methoxy group is cleaved from the anisole to produce radical structure **2a**. Further protonation of structure **2a** yields benzene (structure **2b**).



In pathway 3, the methoxy group is first deprotonated followed by a 2 step radical rearrangement. The deprotonation of anisole produce structure **3a** with a radical on the carbon atom. In a 2 step radical rearrangement, the oxy group shifts to the end to produce structure **3c**. The protonation of structure **3c** yields phenylmethanol (structure **3d**) which is further dehydroxygenated to produce structure **3e**. Finally, protonation of structure **3e** yields toluene (structure **3f**).



Pathway 4 initiates with the protonation of anisole at the $C_{\text{aromatic}}-\text{OCH}_3$ position to produce structure **4a**. This reaction step is possible due to aqueous medium in which the reaction is occurring. There are enough hydrogen ions in the system for this reaction to occur. Structure **4a** then dissociates to yield structure **4b** (benzene) and methoxy radical.

3. Computational Insight

The density functional theory (DFT), which is based on the Hohenberg-Kohn theorem [23], has become an important tool in computational study across the world. The DFT provides us an approximate solution to the Schrödinger's equation by considering the overall electron density of all particles. The density functional theory does not consider individual particles and corresponding charges, as done in waveform method. This approximation reduces the variable from $4N$ (as considered in the waveform method where N is the number of electrons) to only 3 spatial coordinates of the overall electron density [24]. Kohn-Sham applied this simplification to the Schrödinger's equation to give the DFT as we know it today [25]. The reduction in the number of variables has reduced the number of calculations considerably. This makes it possible to solve the Kohn-Sham equation and obtain the energy for moderate systems with current computational resources. To account for the unknown exchange correlation potential ($V_{xc} = f(E_{xc})$) in the solution of Kohn-Sham equation, the E_{xc} is approximated by using different functionals depending on the system [26]. These approximations are formulated by various researchers and are parameterized using experimental data. Several such functionals are available to determine the ground state energy of the system such as B3LYP, B3PW91, ω B97X-V, M06-2x and others. However, the lack of universal global functional makes the selection of functionals difficult for an end-user. In a study conducted by Simon & Goodman [27], over a dozen different functionals are compared to determine the most accurate functional for specific system. Simon and Goodman report that B3LYP can be a reliable functional for predicting the energy of organic reactions. Therefore, in this study, all the simulations are conducted using B3LYP [28] functional. To account for the aqueous phase, the SMD solvation model developed by Truhlar et al. [29] has been used along with B3LYP functional. In the SMD model, the solute is encapsulated in a vacuum shell. The structure of this vacuum shell is determined by superimposing atom centered spheres with a radius approximate to the Van Der Walls radius for each atom. Outside this cavity is the solvent which is defined by a polarized medium. This polarization is defined using the dielectric of the solvent using non-homogenous Poisson's equation (NPE). The potential arising from the mutual interaction of the solute molecules and the polarized continuum is calculated using the NPE and incorporated in the Hamiltonian which is further used to solve the Kohn-Sham equation.

In this study, all the structures are geometrically optimized at B3LYP/6-311+g(d,p) level of theory with SMD solvation model to determine the minimum energy configuration. The optimized molecular

geometry of all structures are given in Figure 1. The bond dissociation energy (BDE) analysis is conducted on anisole at the same level and it is calculated as:

$$\text{BDE} = H_{298}(\text{A-B}) - H_{298}(\text{A}) - H_{298}(\text{B})$$

where H_{298} represents the enthalpy and A-B represents the molecule anisole, A represents the cleaved anisole and B represent the radical which is cleaved from anisole. The vibrational frequency analysis is also conducted for all structures to ascertain true ground state at the same level of theory. Structures having exactly one imaginary frequency are considered to be transition state structure. To further confirm the transition state, intrinsic reaction coordinate (IRC) analysis is conducted on the transition state structure which further links the transition state structure to its two minima – the reactant and the product. All the quantum calculations are performed using Gaussian 09 [30] software package with the aid of GaussView 05 [31] visualization tool.

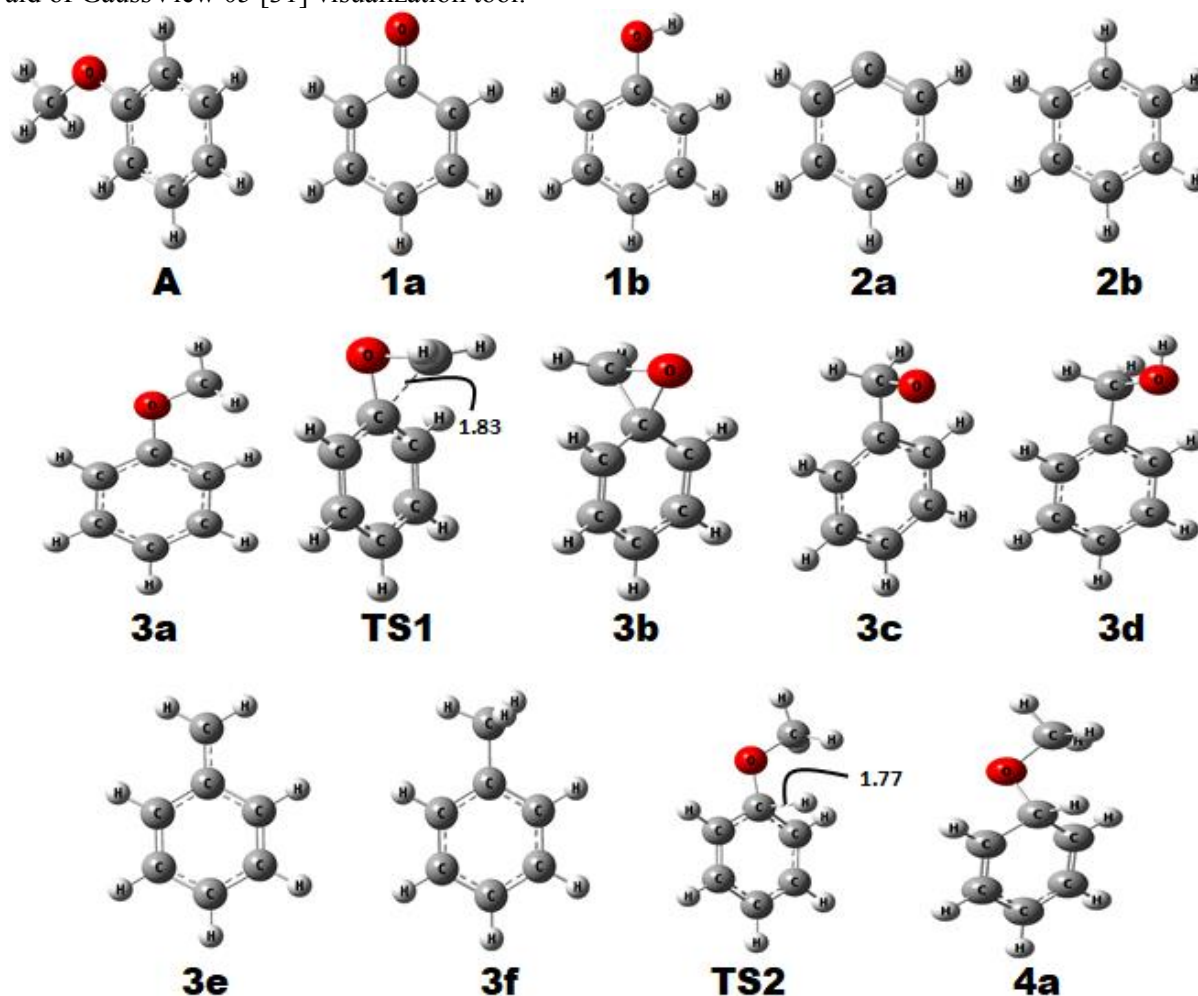


Figure 1: Optimized molecular geometry of all structures

4. Results and Discussion

The BDE analysis of anisole and the reaction kinetics of all pathways along with the thermochemistry of all conversions are discussed below.

4.1. Bond Dissociation Energy

Since anisole is considered a model compound, it is assumed here that there are no other species present in the aqueous medium other than anisole. Thus, to initiate a reaction, the bond dissociation energy analysis plays a vital role. The BDE of anisole in aqueous phase shows (Table 1) that the

breaking of $\cdot\text{CH}_3$ (D2) from the methoxy group of the compound is least energy demanding (55.61 kcal/mol) which is in agreement with the work of Haoquan et al. [32] and Gu et al. [21]. This is followed by the cleaving of the methoxy group (D3) from anisole which requires 89.51 kcal/mol. The breaking of $\cdot\text{H}$ from the methoxy group (D1) is the third least energy demanding breakage with requirement of 98.22 kcal/mol. Rest all other bonds have BDE requirement above 110 kcal/mol and are not likely to occur at moderate conditions. The order of bond dissociation energy requirement is $\text{D2} < \text{D3} < \text{D1} < \text{D7} < \text{D5} < \text{D4} < \text{D6} < \text{D8}$.

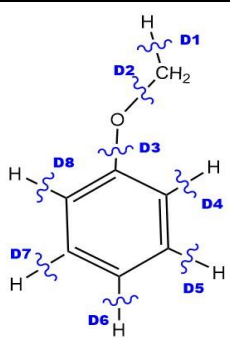
	Bond Cleavage	BDE (kcal/mol)
	D1	98.22
D2	55.61	
D3	89.51	
D4	112.33	
D5	111.73	
D6	113.09	
D7	111.30	
D8	113.62	

Table 1: Bond Dissociation Energy (BDE) of Anisole.

4.2. Reaction Energetics

4.2.1. Phenol formation. In pathway 1, the formation of phenol from anisole initiates by scission of methyl group via pathway 1. Since it is well known that bond dissociation and radical recombination reactions do not involve any intermediate transition state, the energy requirement is calculated using BDE. The BDE analysis shows that the energy requirement for this scission is 55.61 kcal/mol at 298 K to produce structure **1a**. Though this energy is higher than the general catalytic energy requirement of anisole decomposition, it is low enough for the reaction to proceed non-catalytically. Further hydrogenation of structure **1a**, as can be seen from the potential energy surface (PES) curve in Figure 2, is an exothermic step which releases 84.37 kcal/mol of energy to produce phenol.

4.2.2. Benzene formation. The BDE analysis shows cleavage of methoxy group to be the second highest energy demanding bond scission. Thus, pathway 2 requires activation energy of 89.51 kcal/mol to cleave methoxy group from anisole and produce structure **2a**. Structure **2a** is further hydrogenated to produce benzene. The scission of methoxy group is the rate determining step for this reaction pathway. However, in pathway 4, the reaction initiates with the hydrogenation of anisole at the first aromatic carbon atom. This step is feasible due to the occurrence of reaction in the aqueous medium. Sufficient hydrogen radicals are present above the coulomb barrier for the reaction to occur. The protonation of anisole requires an activation energy of mere 5.58 kcal/mol to produce structure **4a** via a transition state **TS1**. This energy is much lower than some of the other gas phase catalytic works [21,22]. The structure **4a** further dissociates to form benzene and $\cdot\text{OCH}_3$ releasing 2.44 kcal/mol of energy.

4.2.3. Toluene formation. The cleavage of $\cdot\text{H}$ from the methoxy group of anisole, which requires 98.22 kcal/mol, initiates pathway 3 to produce structure **3a**. This energy requirement is high and hence the reaction is most likely not to occur at moderate conditions. Structure **3a** then undergoes radical rearrangement in 2 steps via transition state **TS1** which requires 12.48 kcal/mol of energy to cross the activation barrier and produce structure **3c**. Hydrogenation of structure **3c** produce phenylmethanol and release 103.64 kcal/mol of energy which is further dehydroxygenated and hydrogenated simultaneously by providing 73.82 kcal/mol of energy to produce toluene.

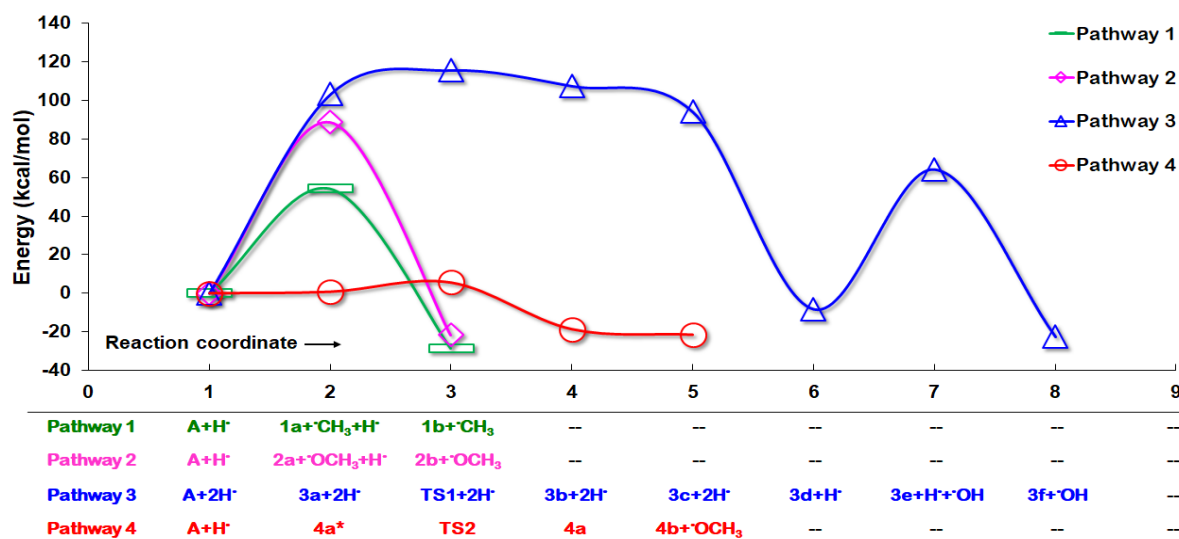


Figure 2: Potential energy surface curve for all reaction pathways.

4.3. Thermochemistry

The thermochemical parameters (Gibb's free energy change (ΔG) and enthalpy change (ΔH)) for each reaction pathway is calculated for 298 K, 398 K and 498 K at atmospheric pressure. The thermochemical parameters are same for pathway 2 and 4 since the reactants and products are same for both the pathways. In pathway 1, free energy change is -31.97 kcal/mol which is quite favourable at 298 K and with increase in temperature, the favourability increases. The enthalpy change is also favourable and not much affected by the temperature. It is calculated to be -28.75 kcal/mol at 298 K and decreases to -28.95 kcal/mol at 498 K. The equilibrium rate constant (K_{eq}) is also favourable (see Figure 3). In pathway 2 and 4, the ΔG is calculated to be -26.57 kcal/mol at 298 K which decreases to -29.12 kcal/mol signifying favourability with increase in temperature. The temperature also has a positive impact on the ΔH which decreases from -22.39 kcal/mol at 298 K to -23.28 kcal/mol at 498 K. Pathway 3 also exhibits similar trend where increase in temperature increases the spontaneity. ΔG for pathway 3 is found to be -25.31 kcal/mol and $\Delta H = -22.65$ kcal/mol at 298 K which decreases to -26.99 kcal/mol and -23.04 kcal/mol at 498 K respectively.

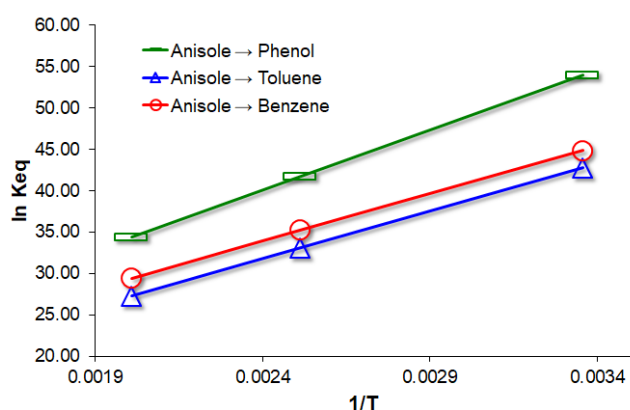


Figure 3: $\ln K_{eq}$ vs $1/T$ graph for all conversions

5. Conclusion

In this work, a DFT study is conducted considering anisole as a bio-oil model compound to determine the thermochemical parameters of the upgrading of anisole to platform chemicals. First, a BDE

analysis is conducted for anisole to determine the energy requirement for the breakage of bond to initiate the reaction. Consequently three different pathways are proposed to produce phenol, benzene and toluene. Also, since the medium of reaction is aqueous, a pathway proposing direct hydrogenation of anisole is also hypothesized to yield benzene. It is observed that the direct hydrogenation of anisole at C_{aromatic}-OCH₃ position requires only 5.58 kcal/mol which is comparable to the energy barriers observed in catalytic reactions. Thus, the formation of benzene is most likely to proceed via pathway 4. Also, as per this study, benzene is likely to be the major product. The formation of phenol is the second most energy demanding reaction with the rate limiting step requiring 55.61 kcal/mol. However, the formation of toluene is less likely to proceed at moderate condition due to the high activation energy. The thermochemical parameter show favourability for all pathways and hence all the reactions are spontaneous and feasible.

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