International Journal of Basic and Applied Chemical Sciences ISSN: 2277-2073 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jcs.htm
2015 Vol. 5 (3) July-September, pp.17-23/Bosire et al.

Research Article

MOLECULAR MODELING OF FURAN FROM THE THERMAL DEGRADATION OF SCRAP TYRES

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ABSTRACT

The atmosphere is the dominant transport pathwayfor many chemicals of mounting environmental concern including those from municipal waste incineration, tobacco burning, fireworks, and aviation, war, and forest fires. Tyre burning is one of the most conventional methods of waste management amid the clinical consequences widely reported in literature. This study therefore examines furan as one ofthe common hazardous molecular by-products of tyre burning known to be carcinogenic as well as a hepatoxic. Currently, there are limited studies on the molecular behavior of furan in the environment hence this study is necessary. To mimic actual tyre burning conditions, a waste tyre sample (5g) was burned under atmospheric conditions in an air depleted environment in a thermal degradation reactor and the smoke effluent was passed through a transfer column. The pyrolysis effluent was sampled into a crimp top vial and analyzed using Gas Chromatography (GC) hyphenated to a mass selective detector (MSD). To explore the mechanistic behavior of furan, Density Functional Theory (DFT) analytical gradient was employed. It was clear form experimental data that the yields of furan from tyre burning reached a maximum at about 400˚C. On the other hand, it was noted form theory that the formation of furanyl-type radicals from furan is not thermodynamically favored. The possible decomposition channels of furan have also been presented in this study.

Keywords: *Atmosphere, Density Functional Theory, Thermal Degradation, Scrap Tyre*

INTRODUCTION

There is a threat to safety in environmental and biological health posed by indiscriminate burning of waste tyres in urban towns in both developed and developing countries. For instance, it is reported in literature that in 2003, the United States of America (USA) produced nearly 290 million scrap tyres (Eilhan and Marco, 2009). This was a huge environmental challenge since the combustion of burnable materials such as tyre waste generates various products in smoke which may diminish light, obscure vision, in addition to the fact that its gaseouscomponents and particulate matter could be highly toxic as well as carcinogenic (Chaturvedi, 2010). Developing countries in particular, have been the epitomeof several investigationsof health outcomes of municipal waste incineration, tobacco smoke, wild fires, and tyre burning. Accordingly, air quality improvement is key in prevention of adverse health consequences (Isabella *et al.*, 2013). Biological health damage may take the form of asthma, bronchitis, reduced lung capacity, or unspecific functional changes, and cell aberrations (Chaturvedi, 2010; Ghose, 2009). A common response to atmospheres containing combustion by-products is lung oxidative stress, coronary heart disease, emphysema, and consequently cancer. This may be due to the generation of reactive oxygen species (ROS), oxygen containing compounds including furans, dioxins, superoxides, peroxides, and hydroxyl radicalsbecause modification of biomolecules by free radicals and other active oxygen species is an ongoing process in all living cells (Becker *et al.*, 2005; Campos *et al.*, 2011). As a matter of fact, aromatic heterocyclic compounds such as furan are emitted during fossil fuel and biomass combustion, and have been identified as air pollutants (Saggese *et al.*, 2013). Therefore, this study will attempt to develop an environmental model on the toxicity and possible carcinogenicity of furan from tyre burning and extrapolate it to other combustion sources.

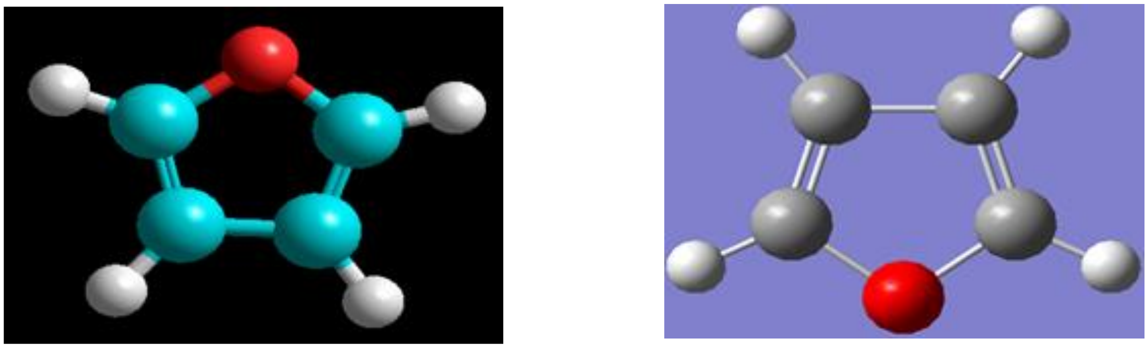

Figure 1: Structures of molecular furan modeled using HyperChem (left) and Gaussian (right) computational soft wares

The furan molecule (Figure 1) belongs to a series of the five-membered heterocyclic compounds which are relevant in biochemistry and also in industry (Saggese *et al.*, 2013; Dampc and Zubek, 2008). Its heterocyclic structure incorporates an oxygen atomand has a high degree of aromaticity (Dampc and Zubek, 2008). Furans are also derived from biomass decomposition and conversion of biomass to fuels and high-valued chemicals is an increasingly important alternative to the non-renewable resources of energy (Organ and Mackie, 1991).

The Thermal decomposition and air pollutant generation mechanisms of tyres due to their heterogeneous constituents: natural rubber, poly-isoprene, sulphur, and reinforced material, is poorly understood (Eilhan and Marco, 2009). Compared to conventional fuels, tyre pyrolysis has a higher possibility of enhancingPAH formation but under oxidative conditions, oxygenated compounds including furan are also formed. Whereas polycyclic aromatic hydrocarbons (PAHs) from tyre burning have been extensively studied, no such studies have been conducted on furan. The principal focus of the current study is to determine the presence of furan in the combustion of tyre waste and subsequently develop an environmental model for its carcinogenicity and other medical effects. This contribution elucidates quantum mechanically the formation of pyrolytic products of furan and their toxic nature. The mechanistic pathways are modeled and their energetics determined in order to evaluate their favourable formation in the environment. Modeling and thermochemical considerations of furan led to the postulate that the initiation of pyrolysis takes place by C-Obond scission to a very unstable bi-radical which can undergo decomposition, via parallel reaction paths, to the observed by-products (Organ and Mackie, 1991; Lifshitz *et al.*, 1986). Previous research has shown that furan undergoes unimolecular decomposition to form carbon monoxide, ketene, propyne, propargyl, and formyl radicals (Dampc and Zubek, 2008; Lifshitz *et al.*, 1986; Urness *et al.*, 2013). In addition to these mechanistic channels, this study will investigate the energetics for the formation radical intermediates; furanyl and 2-furanyl radicals which may be responsible for oxidative stress, cardiac problems, and possible neuronal diseases such as Parkinson's disease (Majima and Toyokuni, 2012). These dissociation products involve cleavage of several bonds and possibly creation of new bonds (Dampc and Zubek, 2008).

MATERIALS AND METHODS

Computational Methodology

All density functional theory (DFT) calculations were performed using the Gaussian 03 suite of programs (Frisch *et al.*, 2004). The Geometries were optimized at B3LYP/6-311+(d,p) level of theory (Zhang *et al.*, 2010). Diffuse and polarization functions are included on heavy atoms because they are especially necessary in the optimization of large systems and radicals; polarization functions were also added on hydrogen atoms in order to account for the presence of hydrogen-bonds (Saron *et al.*, 2008). All stationary points were determined by a frequency analysis from which zero-point energy and thermal corrections were attained using the ideal gas approximation and standard procedures (Saron *et al.*, 2008). Quantum chemical calculations are critical in providing new insights on plausible mechanisms on the thermal decomposition of environmental pollutants. Energy values for gas-phase optimizations reportedin this study includethermal free energy corrections at 298 K and 1 atm. The Van der Wall's was determined quantum mechanically using DFT.

Sample Preparation and Experimental Protocol

Waste tyre (YANA 155R13, F-570) was sampled from a tyre waste yard in Nakuru town, Kenya. The waste tyre was sliced and a clean portion of it was taken for combustion analysis in the laboratory. 5 mg of sliced tyre was accurately weight to ±0.2 mg and packed in a quartz reactor of dimensions: i.d. 1 cm x 2 cm (volume ≈ 1.6 cm^3). The tyre sample in the quartz reactor was placed in an electrical heater furnace whose maximum heating temperature is 1000 ˚C. The heater (muffle furnace) was purchased from Thermo Scientific Inc., USA. The tyre sample was burned in an airdepleted atmosphere in a quartz reactor and the smoke effluent was allowed to pass through a transfer column and collected in 2 mL crimp top amber vials for a total pyrolysis time of 2 minutes. This combustion experiment was conducted under conventional pyrolysis described elsewhere (Kibet *et al.*, 2012) and the evolution of furan was monitored between 300 and 550 ˚C. The experimental set up for this investigation is presented in Figure 2.

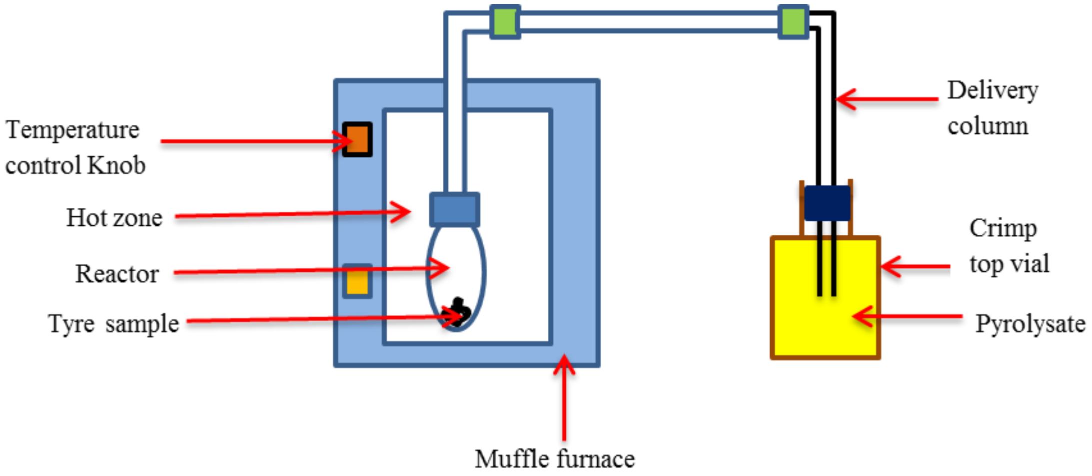

Figure 2: Experimental set-up for monitoring the evolution of hazardous by-products from tyre waste

GC-MS Characterization Waste tyre Sample

The organic by-products from the waste tyre burning were investigated using Agilent 6890 Gas chromatograph hyphenated to an Agilent mass selective detector (MSD), 5890 series. 1 uL of sample was injected into a GC column (HP-5MS, 30m x 250 um x 0.5 um). The temperature of the injector port was set at set at 150 ˚C to enable the conversion of organic components to the gas-phase prior to MS analysis. Temperature programming was applied at a heating rate of 15˚C for 10 minutes, holding for 1 minute at 200˚ C, followed by a heating rate of 25 ˚C for 4 minutes, and holding for 10 minutes at 300 ˚C. Electron Impact ionization energy of 70 eV was used. Furanwas identified using National Institute of Science and Technology software (NIST, USA) (Kibet *et al.*, 2012). This was confirmed by comparing the peak shape and the retention time of furan with that of pure furan (standard).

RESULTS AND DISCUSSION

The yield distribution of furan from tyre burning is presented in Figure 3 *vide infra*. It is evident thatfuran peaks between 400 and 500 ˚C. This coincides with the temperature region where most biomass/fuel materials are considered to release most of their by-products. At temperatures as low as 400 ˚C, the concentration of furan is low. The GC-Area counts of furan at 500 ˚C was 1.09 x 10^8 while at 300 ˚C it intensity was found to be 2.5 x 10^7. Clearly, the yields of furan at low temperatures are very small. Equally, at temperatures above 500 ˚C, the yields of furan begin to decrease. This is expected because above 500 ˚C, aromatic hydrocarbons begin to form and few oxygenated compounds can form above this temperature. The evolutions of furan with increase in temperature is therefore critical in understanding the optimum temperature of release and possibly assist in designing incinerators that can burn biomass waste at low temperatures thereby avoiding high release of poisonous compounds to the atmosphere.

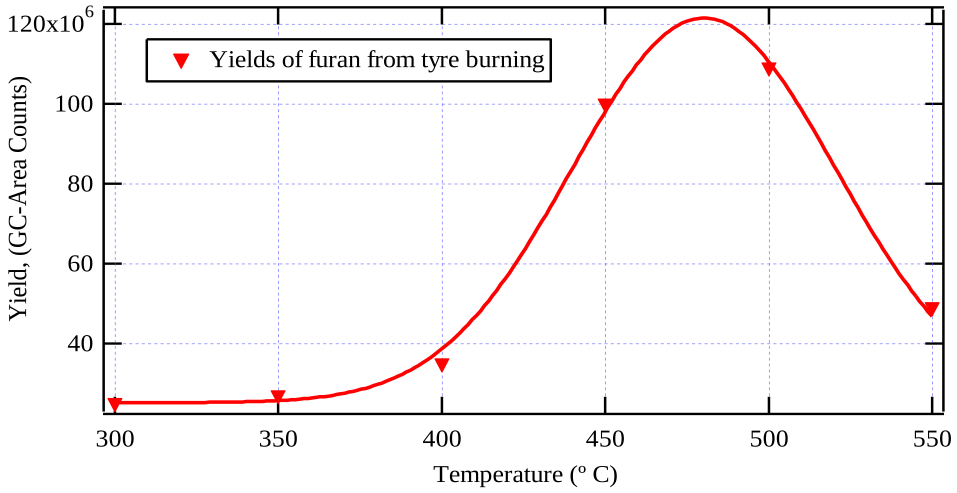

Figure 3: Product distribution of furan form combustion of tyre waste

The Proposed Mechanistic Degradation of Furan

Figure 4 represents the mechanistic pathways of the thermal degradation of furan as reported in literature (Saggese *et al.*, 2013) and in this study. The principal focus was to explore the energetics of each pathway and consequently the most favorable channel for the thermal degradation of furan.

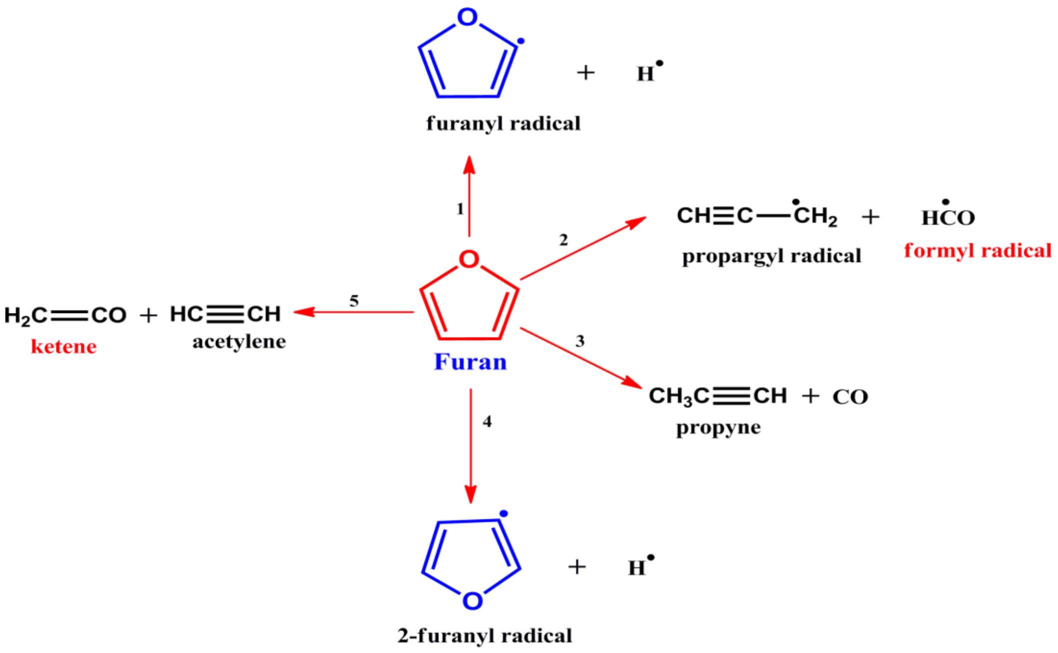

Figure 4: Possiblemechanistic channels for furan degradation

Figure 5 gives the thermodynamic considerations conducted to determine the energetics of the thermal decomposition of furan into possible bio-hazardous by-products. It is clear that the conversion of furan to ketene and acetylene (Rxn 5) as predicted in Figure 5A is the most favorable decomposition route of furan.

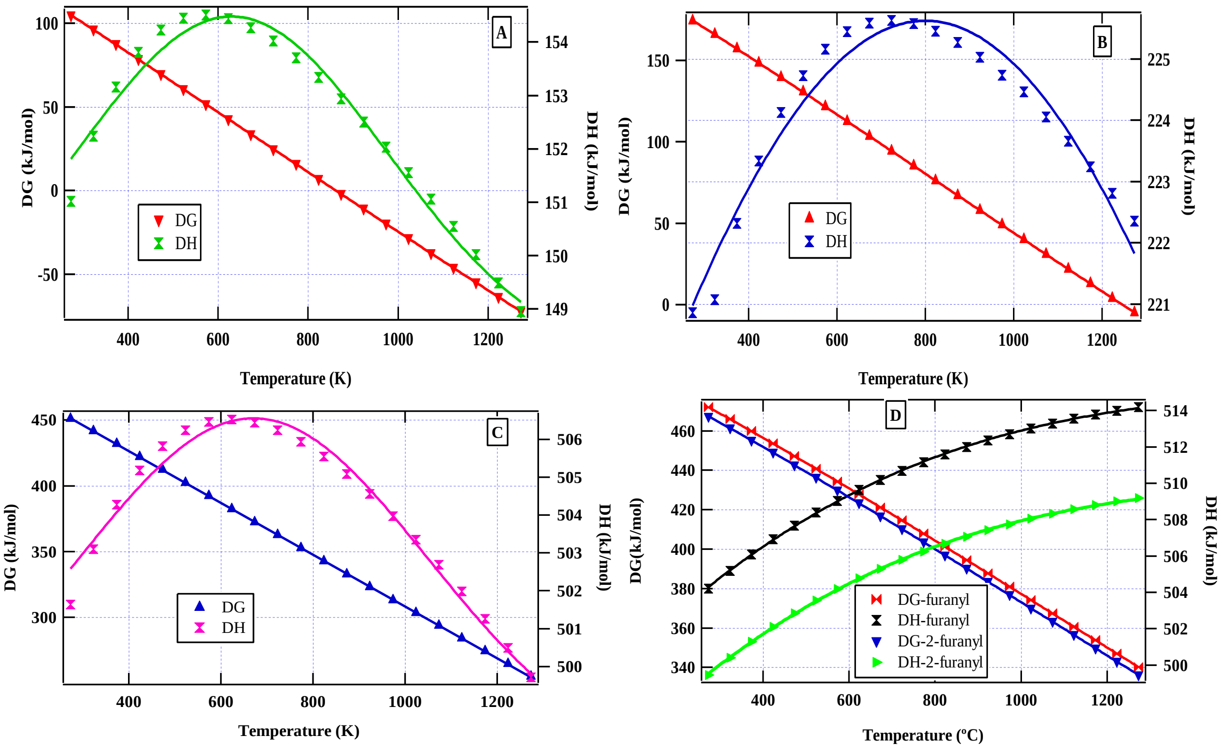

Figure 5: Thermodynamic parameters for the thermal degradation of furan

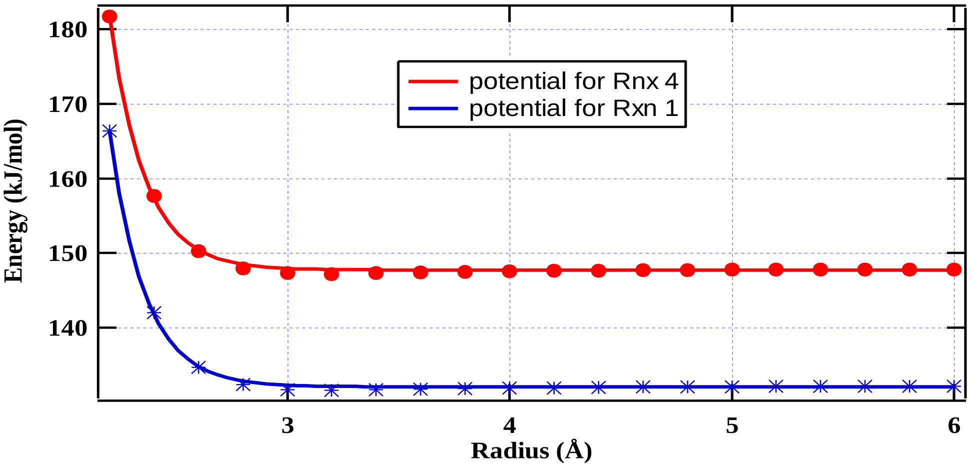

Figure 6: The Van der Wall's potential for the formation of furan from furanyl based-radicals

This is because such a route is accompanied low ΔG values. Thermodynamically, the lower the ΔG values, the more feasible a reaction is. This will also imply from Figures 5B and Figure 5C that the transformation of furan according to Rns 2 and 3 are also favored but to a less extent compared to Rnx 5. Rxns 1 and 4 are the least favored and may not actually occur. From the theoretical calculations presented in this work, only small amounts of either 1-furanyl or 2-furanyl radicals are possibly produced at high temperatures. It is nonetheless evident that during the thermal degradation of furan via various mechanistic channels, the change in enthalpy first increases before decreasing significantly at a certain temperature (Figure 5). For instance, the change in enthalpy for Rxn 5 increases from 298.15 K to 623 K before decreasing exponentially. Similarly, reactions for 2 and 3, the change in enthalpy increases from 298.15 K to respectively 723 and 623 K before decreasing (Figures 5B and 5C). Generally, this implies that at high temperatures, Rxns 2, 3 and 5 become less endothermic. Interestingly, Rxns 1 and 4 do not exhibit the same behavior because the formation of furanyl radicals are not thermodynamically favored (Figure 5D). To further justify that these reactions (Rxn 1 and 4) rarely occur even at high temperatures, their Van der Wall's potentials were examined and presented in Figure 6. This curve (Figure 6) does not give a definite potential well suggesting that the attractive forces between furanyl radical and the hydride are minimal and thus such a reaction does not possibly take place. This is consistent with thermodynamic data which indicate that large amounts of heat must be absorbed for reactions 1 and 4 to take place. Moreover, theΔG values are very high and thus the reactions are not feasible at ordinary temperatures. The approximate potential wells for the furanyl radicals occur at 2.8 Ǻ but at different energies (132.36 and 147.98 kJmol^{-1}for 2-furanyl and 1-furanyl radicals respectively).

Conclusion

Furan emissions from municipal waste incineration especially from tyre waste have been investigated in this work. Consequently, the highest level of furan emissions was noted between 400 and 500 ˚C. To complement experimental work, detailed theoretical calculations were performed on furan. Remarkably, it was noted that furan is a very stable molecule and the possibility of forming furanyl-type radicals at ordinary temperatures is rare. To confirm that furanyl type-radicals are seldom formed under pyrolytic conditions, the Van der Wall's potential form furanyl-based radicals and hydride radical was explored. Accordingly, the potential wells formed were non-specific as repulsive forces dominated the attractive forces. Nevertheless, furan can decompose to ketene and acetylene, or propargyl radical and formyl radical at fairly low temperatures. These routes were found theoretically to be the major decomposition pathways of furan and are consistent with literature surveys.

ACKNOWLEDGEMENT

The authors wish to thank the division of Research and Extension (R&E) at Egerton University for funding this study. Dr. Moses Lagat of the University of Surrey, UK is greatly appreciated for analysis of furan from tyrepyrolysate.

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