Chemical characterization of gaseous species from the pyrolysis process using scrap tires

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Abstract

Particle exposure can lead to a variety of health effects. For example, numerous studies link particle levels to increased hospital admissions and emergency room visits – and even to death from heart or lung diseases. Scrap tire combustion releases several toxic air pollutants. This study assessed the generation of H_2, N_2, CO, H_2S and nine aliphatic compounds, namely CH_4 (Methane), C_2H_2 (Acetylene), C_2H_4 (Ethylene), C_2H_6 (Ethane), C_3H_6 (Propylene), C_3H_8 (Propane), C_4H_8 (Butene), C_4H_{10} (Butane), C_5H_{12} (Pentane) generated in a used-tire pyrolysis process and the aliphatics removal by a wet scrubber (WSB) and a flare. CH_4, H_2, N_2 and C_2H_6 were found to be major gaseous species in pyrolysis emissions with the percentage contributions to total sum of gaseous species of 33.18%, 15.62%, 12.23% and 8.69% respectively.
Keywords: scrap tires, aliphatics, pyrolysis, air quality.

1 Introduction

Anthropogenic activities in any megacities are known to increase particulate matters in the atmospheric environment. Among them, the fine particles (particles size smaller than 10 micron, PM_{10}) have been shown their impacts on human's respiratory tract. According to the Pollution Control Department of

WIT Transactions on Ecology and The Environment, Vol 174, © 2013 WIT Press
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/AIR130231

Thailand (PCD) standard, There are two PM 10 standards, a 24-hour standard and an annual standard. These standards are:

- 120 micrograms per cubic meter (ug/m^3) for the 24 hour standard
- 50 micrograms per cubic meter (ug/m^3) for the annual standard

One of the most important components of the PM_{10} is persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs) and dioxins, which are widely acknowledged as carcinogens and mutagens that originated from incomplete combustion of hydrocarbons. Because of its property as a carcinogen, World Health Organization (WHO) set PAHs (expressed as a concentration of benzo[a]pyrene), safety limit at 1 ng m^{-3} [1–4]. POP concentrations on PM_{10} are varied according to the combustion condition and fuel type, therefore, emission source type could lead to cancer in human. Among various emission source types of POPs, the burning of scrap tires will be of particular concerns due to the rapid increasing vehicles on road, which will inevitably produce large amounts of scrap/waste tires.

According to the information provided by department of land transport, the total number of registered vehicles in 2000 including motorcycle, tricycle, van and pick up, bus, truck, trailer and automobile's trailer in Bangkok and out of Bangkok were 4,468,977 and 16,229,802 respectively. It is also worth mentioning that the registered vehicle number shows increasing trend with relatively high correlation coefficients (R^2) for motorcycle (R^2), van and pick up (R^2), car (R^2) and others (R^2). As a consequence, National Energy Policy Office (NEPO) had estimated the final energy demand in the business-as-usual case of five business sectors namely transport, residential, industrial, agricultural and commercial as 64.67, 19.75, 65.25, 3.47 and 5.72 MTOE (Million Tonnes of Oil Equivalent) respectively. Recently, over 550,000 ton of tires were produced per year in the Thailand and this figure was similar in the EU countries and USA [5]. Without any doubts, Thailand requires more alternative fuel resources coupled with green technology for disposal and recycling these waste tires as a result of high production/consumption of tries.

During the past few years, several studies have been carefully investigated the applications of pyrolysis as an alternative green technology to convert waste automotive tires into crude oil and carbon black [6 − 8]. Despite this fact, only few researches focus on the emissions of air pollutants from converting scrap tires to crude oils during the heating process [9 −10]. Therefore, it is crucial to assess the emissions of air pollutants from the thermochemical decompositions of used tires. This study aims to both qualitatively and quantitatively identify gaseous species from emissions of pyrolysis plants at Wanornnivas Agriculture Cooperative, Sakon Nakhorn Province, Thailand.

Table 1: Type of vehicles registered at department of land transport, Thailand (30/09/2011).

Type of Vehicle	Number of Vehicles
Sedan (Not More Than 7 Pass.)	4,928,192
Microbus and Passenger Van	401,839
Van and Pick Up	5,103,772
Motor Tricycle	1,418
Interprovincial Taxi	4
Urban Taxi	102,585
Fixed Route Taxi	3,392
Motor Tricycle Taxi (Tuk Tuk)	21,160
Hotel Taxi	1,817
Tour Taxi	804
Car For Hire	66
Motorcycle	17,897,524
Tractor	268,170
Road Roller	10,425
Farm Vehicle	90,189
Automobile Trailer	2,467
Public Motorcycle	136,425
Bus	132,749
Truck	843,395
Small Rural Bus	4,289

Source: Department of Land Transport (2011).

2 Methodology

2.1 Sampling site descriptions and monitoring period

To investigate the chemical compositions of emissions from thermochemical decompositions of scrap tires and pyrolysis activities, trace gaseous species were collected at the pyrolysis plant of Wanornnivas Agriculture Cooperative, Sakon Nakhorn Province, Thailand. Thirteen trace gaseous species, namely H_2, N_2, CO, H_2S, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, C_4H_{10} and C_5H_{12} were monitored every hour.

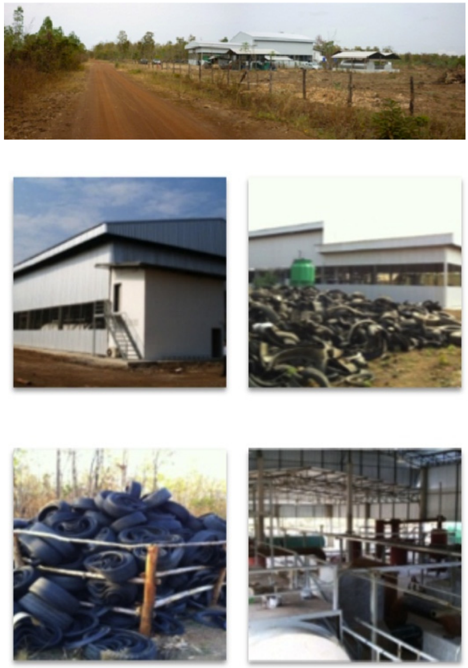

Figure 1: The facilities of pyrolysis plant of Wanornnivas Agriculture Cooperative, Sako Nakhorn Province, Thailand.

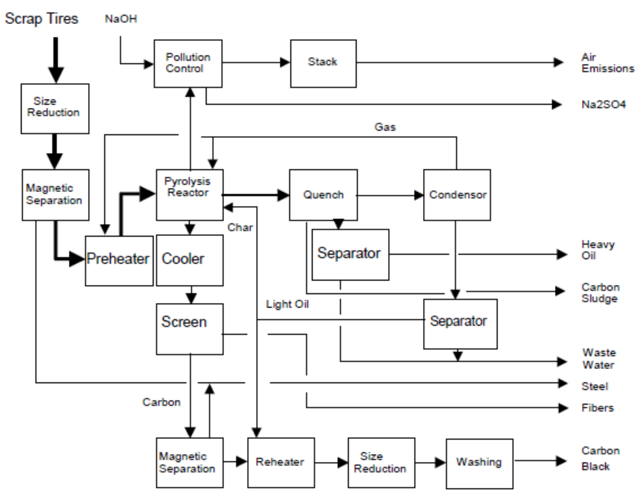

Figure 2: Schematic diagram of pyrolysis process by using scrap tires.

Figure 3: Pyrolysis systems at Wanornnivas Agriculture Cooperative, Sako Nakhorn Province, Thailand.

2.2 Materials and methods

2.2.1 Analysis of trace gaseous species

All trace gaseous species were both qualitatively and quantitatively identified on the basis of 1996 Compressed Natural Gas as Vehicle Fuel. This Standard regulates the technical requirements on compressed natural gas as vehicle fuel by referring to ISO/ FDIS 15403 and was brought forward by China National Petroleum Corp. (CNPC).The methane number of a gas fuel is determined with ASTM octane number determination method, and by comparing the detonation trend of this fuel with standard fuel compounds in standard engine test under regulated conditions. When the anti-detonation performance of the tested gas fuel is the same as that of standard fuel mixed by methane and hydrogen according to some certain proportion, the value of volume percentage of methane in this standard fuel shall be the methane number of this gas fuel.

Table 2: Analytical methods for trace gaseous species.

Test Item	Analytical Method
Hydrogen	GB/T 13610 -2003
Nytrogen	GB/T 13610 -2004
Methane	GB/T 13610 -2005
Ethane	GB/T 13610 -2006
Ethylene	GB/T 13610 -2007
Acetylene	GB/T 13610 -2008
Propane	GB/T 13610 -2009
Propylene	GB/T 13610 -2010
Isobutane	GB/T 13610 -2011
Normal butane	GB/T 13610 -2012
1-butene	GB/T 13610 -2013
Along-2-butene	GB/T 13610 -2014
counter-2butene	GB/T 13610 -2015
Isopentane	GB/T 13610 -2016
N-pentane	GB/T 13610 -2017
Total Pentane	GB/T 13610 -2018
Carbon monoxide	GB/T 13610 -2020
Hydrogen sulfide	ASTM D4810-88

2.2.2 Determination of pyrolysis oil physicochemical properties

2.2.2.1 ASTMD 4052-96 Gravity is basic information that can be applied in conjunction with other physical properties to classify both the light and heavy fractions of pyrolysis oils. Determination of the gravity is essential for the conversion of measured volumes to volumes at the standard temperature of 60ºC. In this study, the standard method ASTM D 4052-96 was applied for the determination of gravity.

2.2.2.2 ASTM D445-06 Viscosity is one of important physical parameters which are mostly used as index for the estimation of handling, optimum storage and operational conditions. Therefore, the accuracy of analytical method of viscosity is crucial to many product specifications. This analytical method indicates a process for the measurement of the kinematic viscosity, ν, of pyrolysis oils, both transparent and opaque, by determining the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η, can be obtained by multiplying the kinematic viscosity, ν, by the density, ρ, of the liquid. The range of kinematic viscosities covered by this test method is from 0.2 to 300,000 mm^2 s^{-1} at all temperatures.

2.2.2.3 ASTM D4294 Since the amount of sulfur is critically restricted by various regulations promulgated in federal, state, and local agencies, the rapid and precise detection of total sulfur is essentially crucial. In this study, we use ASTM D4294 method to measure sulfur content in pyrolysis oil products. ASTM D4294 includes the measurement of total sulfur in petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquefiable with moderate heat, or soluble in hydrocarbon solvents.

2.2.2.4 ASTM D92 The risk of pyrolysis oils to form a flammable mixture with air can be estimated by the determination of flash point. Several benefits of measuring flash point are i) safety regulations to define flammable and combustible materials, ii) indicator of the possible existence of highly volatile and flammable materials in a relatively nonvolatile or nonflammable material, iii) risk assessment of the fire hazard of a particular end use. ASTM D92 explains the quantification of the flash point and fire point of pyrolysis oil products by a manual Cleveland open cup apparatus or an automated Cleveland open cup apparatus. In addition, the test method is applicable to all petroleum products with flash points above 79ºC and below 400ºC with the exception of fuel oils.

2.2.2.5 ASTM D1826 ASTM D1826 is a standard test method for calorific (heating) value of gases in natural gas range by continuous recording calorimeter. ASTM D1826 includes the measurement with the continuous recording calorimeter of the total calorific (heating) value of fuel gas produced or sold in the natural gas range from 900 to 1200 Btu-standard ft^{-1}. An extensive investigation of the accuracy of the Cutler-Hammer recording gas calorimeter, when used with gases of high heating value, was made by the National Bureau of Standards in 1957 under a research project sponsored by the American Gas Association.

3 Results and discussion

The physical properties of pyrolysis oil samples (i.e. API Gravity at 60 C, Specific Gravity at 15.6 C, Kinematic Viscosity at 40 C mm^2 s^{-1}, Sulfur Content % wt, Flash Point (C), Heating Value (Cal G^{-1})) were illustrated in Table 3.

Table 3: Physical properties of pyrolysis oil products from scrap tires.

Test Item	Test Method	Result
API Gravity at 60 C	ASTM D 4052-96	47
Specific Gravity at 15.6 C	ASTM D 4052-96	0.83
Kinematic Viscosity at 40 C $mm^2 s^{-1}$	ASTM D 445-06	1.80
Sulfur Content %/wt	ASTMD 5433-05	0.83
Flash Point C	ASTM D 92	42
Heating Value Cal G^{-1}	ASTM D 1826	10820

As illustrated in Table 4, pyrolysis oil yields and heating values of pyrolysis oil products ranged from 1980 to 2020 kg and from 7184 to 7266 g cal^{-1} with the average of 2038 ± 74 kg and 7236 ± 40 respectively. No significant differences between heating temperature and pyrolysis oil yield were detected. In addition, it is worth mentioning that the heating temperature plays a minor role on heating value of pyrolysis oil as well.

Table 4: Heating values of pyrolysis oil products in different temperatures with 5 tons of scrap tires under constant pressure of 3 MPa.

No.	Temperature for pyrolysis process (C)	Pyrolysis Oil Yield/Scrap Tires (kg).	Flash Point (C)	Heating Value (g cal^{-1})
1	300	1980	45	7184
2	300	2000	45	7266
3	300	1980	45	7184
1	350	2100	45	7184
2	350	2150	45	7266
3	350	2150	45	7266
1	400	1980	45	7243
2	400	1980	45	7266
3	400	2020	45	7266

The percentage contributions of H_2, N_2, CO, H_2S and nine aliphatic compounds, namely CH_4 (Methane), C_2H_2 (Acetylene), C_2H_4 (Ethylene), C_2H_6 (Ethane), C_3H_6 (Propylene), C_3H_8 (Propane), C_4H_8 (Butene), C_4H_{10} (Butane), C_5H_{12} (Pentane) measured at pyrolysis scrap tire plant at Wanornnivas Agriculture Cooperative, Sako Nakhorn Province, Thailand are given in Table 5.

Methane shows the highest percentage contribution of 33.2% (v/v). Acetylene, Isopentane and N-pentane displays the lowest percentage contributions of 0.01% (v/v), 0.05% (v/v) and 0.05% (v/v) respectively.

4 Conclusions

According to the information provided by department of land transport of Thailand (Table 1), Van and Pick Up (5,103,772) and Sedan (4,928,192) show

Table 5: Percentage contributions of emission pollutants from pyrolysis process by using scrap tires.

Test Item	Percentage Contribution (%)
Hydrogen	15.62
Nitrogen	12.23
Methane	33.18
Ethane	8.69
Ethylene	6.42
Acetylene	0.01
Propane	5.38
Propylene	6.25
Isobutane	2.04
Normal butane	0.86
1-butene	1.86
Along-2-butene	1.66
counter-2butene	1.12
Isopentane	0.05
N-pentane	0.05
Total Pentane	0.1
Total Pentane	0.3
Carbon monoxide	4

the relative high contribution of producing scrap tires. As a consequence, there are rising concerns of scrap tire waste management. In this study, the application of pyrolysis process as illustrated in schematic diagram (Fig. 2) and facilities of pyrolysis plants (Fig. 3) for converting scrap tires into oils was investigated at Wanornnivas Agriculture Cooperative, Sako Nakhorn Province, Thailand (Fig. 1). Chemical characterization of trace gaseous species from pyrolysis process by using scrap tires was performed by using standard analytical method (Table 2). Methane, hydrogen and nitrogen are three gaseous species dominating the emission pollutants with the percentage contributions of 33.2%, 15.6% and 12.2% respectively. In addition, the heating temperature has no significant influences on both yields and heating values of pyrolysis oils.

Acknowledgements

The authors thank Mashucon Public Co. Ltd., and the School of Social and Environmental Development, National Institute of Development Administration for financial support.

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