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Comparative analysis of the Polycyclic Aromatic Hydrocarbons' content (PHAs) in two separate rice husk forms in Iraq

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are harmful compositions developed typically for thermal applications in the atmosphere or amid the pyrolysis of organic fuels. The goal of this research is to compare the polycyclic aromatic hydrocarbons' content (PAHs) in two rice husk's distinctive sorts in southern and northern Iraq via switched phase high-achievement fluid activity utilizing UV and fluorescence detection. Seven species of polyaromatic hydrocarbons (PAHs) in rice husk of (north Iraq) were determined with the concentration: naphthalene (38.6×10^{-3}), acenaphthylene (46×10^{-3}), acenaphthene (98.8×10^{-3}), benzo (a) anthracene (25.22×10^{-3}), benzo (k) fluoranthene (141.88×10^{-3}), benzo(g.h,i) perylene (7.62×10^{-3}), indeno (1,2,3cd) pyrene (46.2×10^{-3}), while Arabian rice husk (south Iraq) contain six species of PAHs with a different concentration, acenaphthylene (84.04×10^{-3}), acenaphthylene (59.8×10^{-3}), benzo (a) anthracene (104.38×10^{-3}), benzo (k) fluoranthene (136.4×10^{-3}), benzo (g.h,i) perylene (7.62×10^{-3}), indeno (1,2,3cd) pyrene (46.2×10^{-3}), highest PAH concentration in two types of rice husk was benzo (k) fluoranthene ,while lowest concentration PAH was benzo (g.h,i) perylene.

Introduction

Oryza sativa Rice is one of the most cereal crops also to steady nourishment for most of the populace of the universe, particularly Asian countries [1]. Approximately 600 million tons are gathered around the world every year [2]. Rice is frequently consumed in cooked food for individuals to get different nutrients, besides, to complement their caloric absorption[3]. As its main product, the paddy rice's milling has almost 70% abdicate of rice (endosperm), although there are a few unconsumed parcels of the rice created, like rice husk (20 %), rice bran (8 %), and rice germ (2 %) [4-6].

A family of Volatile, Semi-Volatile, and Non-Volatile natural species made up of Carbon and Hydrogen particles is believed to be polycyclic aromatic hydrocarbons (PAHs). Essentially, following the fuel particles' devolatilization, they are shaped at the beginning stage of combustion. Upon warming, methane, acetylene, and other natural unstable compounds are somewhat split into littler unsteady free radicals. The radicals face different PAHs with two or more than two aromatic rings [7-9] during recombination. A few PAHs with a more noteworthy number of aromatic rings, or a higher molecular weight such as benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (a) pyrene, indeno [l,2,3-cd]pyrene, dibenzo (a,h) anthracene, are considered to be powerful carcinogens and mutagen [10-12]. PAHs transmitted from combustion frameworks are found in two stages of combustion materials, specifically matter and vaporous stage. Low molecular weight (2- and 3-ring) PAHs are by large related with vaporous combustion items, such as naphthalene, acenaphthylene, phenanthrene, and fluoranthene, while higher molecular weight (4-,5, and 6- ring). PAHs are generally transmitted using fly cinder and sediment particles commonly referred to as matte particles [13-14]. Strategies for the assurance of PAHs within the environment incorporate gas chromatography with fire

ionization detection (GC/FlD) and high —performance liquid chromatography (HPLC) with bright detection. While GC/FlD is the more delicate the method is subject to foundation interferer from other carbonaceous sources.HPLC is the favored strategy of examination since it gives the essential affectability in combination with higher specificity. Two distinctive reversed-phase high-performance liquid chromatography (RP-HPLC) strategies for the assurance of PAHs in extricated natural samples are presented in this application note. Solid tests may be extricated utilizing supercritical fluid extraction (SFE) strategies. Extricates ought to be processed in glass, shielded from light, and refrigerated before RP-HPLC [15-17]study. A large number of studies have been carried out over the past decade on PAH emanations from different combustion frameworks terminating a few biomass fills and (co-) terminating pulverized coal with wood buildup [18-19].

Fig(1) Arabian rice husk(south of Iraq)

Fig(2) Kurdish rice husk(north of Iraq)

Preparation and Storage of Sample

Test taken for PAH investigation ought to be kept in light-protected glass holders and refrigerated before they are removed. Using dichloromethane, PAHs are usually extricated and after that exchanged before the investigation into acetonitrile. The mini-column Sepack 18 solid-phase cartridge was used to collect aqueous tests.

Equipment

Shimadzu LC- 10 AVP HPL system consisting of: Binarygradient system SPD 10 AVP U V -VIS absorbance detector Shimaduz CR6A chroma pack integrator PAH (50x4.6mm LD),3 um particle column super

Reagents:

Acetonitrile, Fisher HPLC Grade Deionized Water, methylene chloride HPLC grade Sepack C- 18 Cartridge column solid phase extract Priority pollutant 1 6 PAH standard from sigma

Method for determination of PAH in rice husk:

l00mg of sample was mixed with 1 L methanol: chloroform (50:50, v/v) agitated for 1 h, keep the mixture to settle down for 3h, then decantation the extract and repeated once, collect the two extract, then concentrated the mixture by evaporation the dissolvable with liquid N2 steam until almost 0.5 ml is reached, at that point include a few of Portable stage to reach 5ml. The mixture was passed through a 2.5 µm disposable filter, at that point, 50 µm were infused on the HPLC column. The intensity for each composite was decided from a quantitative point of view by comparing the crest range of the standard with that of the sample. Temperature regulation is adjusted to guarantee steady maintenance time for gradients, which is also important. Using both UV and fluorescence detection, this strategy was to decide PAHs and it is compatible with U.S. EPA strategies 550 [1] 810 [2] and 8310 [3] in addition to other worldwide regulatory methods.

Pre concentration factor =1000/5=200,
Column: SUPELCOSIL LC-PAH, (150mm×4.6mm),3 µm
Guard :Suelguard LC-PAH(20×4.6mmID)
Temperature:30 0 C
Portable stag:Acetonitrile
Flow velocity:1.5 ml/min
Inj.volume:50 µm UV Detection :254nm

Table (1) concentration PAHs in rice husk

Name of PAH Compounds	**Rt. min**	**Area**	**Con.of standard**	**Con.PAH in (Kurdish)rice husk µg/gm×10^{-2}**	**Con.PAH in (Arabian) rice husk µg/gm×10^{-2}**
Naphthalene	2.89	996381	5	3.86	…
Acenaphthylene	3.33	1851555	5	4.6	8.404
Acenaphthlene	5.63	2106861	5	9.88	5.98
Benzo(a)anthracene	10.64	1576582	5	2.522	10.438
Benzo(k) fluoranthene	14.72	938398	5	14.188	13.64
Benzo (g.h.i) perylene	16.44	601856	5	0.762	0.762
Ideno(1,2,3cd)pyrenen	17.89	1489836	5	4.62	4.62

Concentration of sample µg/ml=Area of sample/Area of standards ×con. of Standard ×1/pre.con.factor(200)

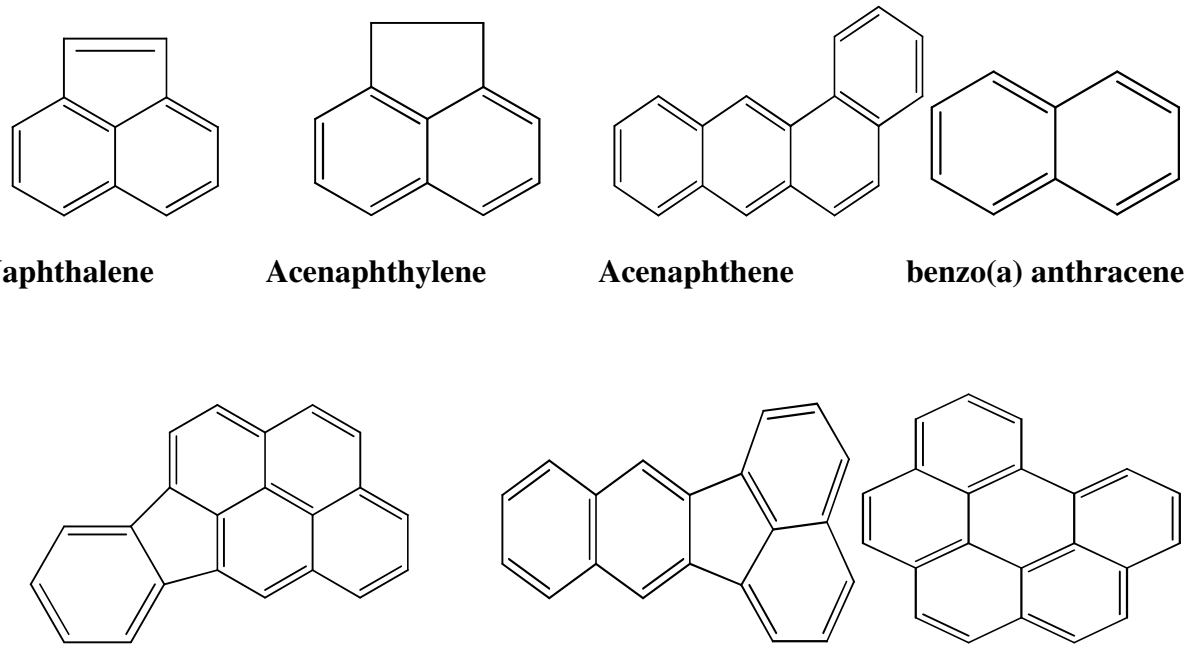

Fig (3) Some of polycyclic Aromatic Hydrocarbons(PAH) in rice husk

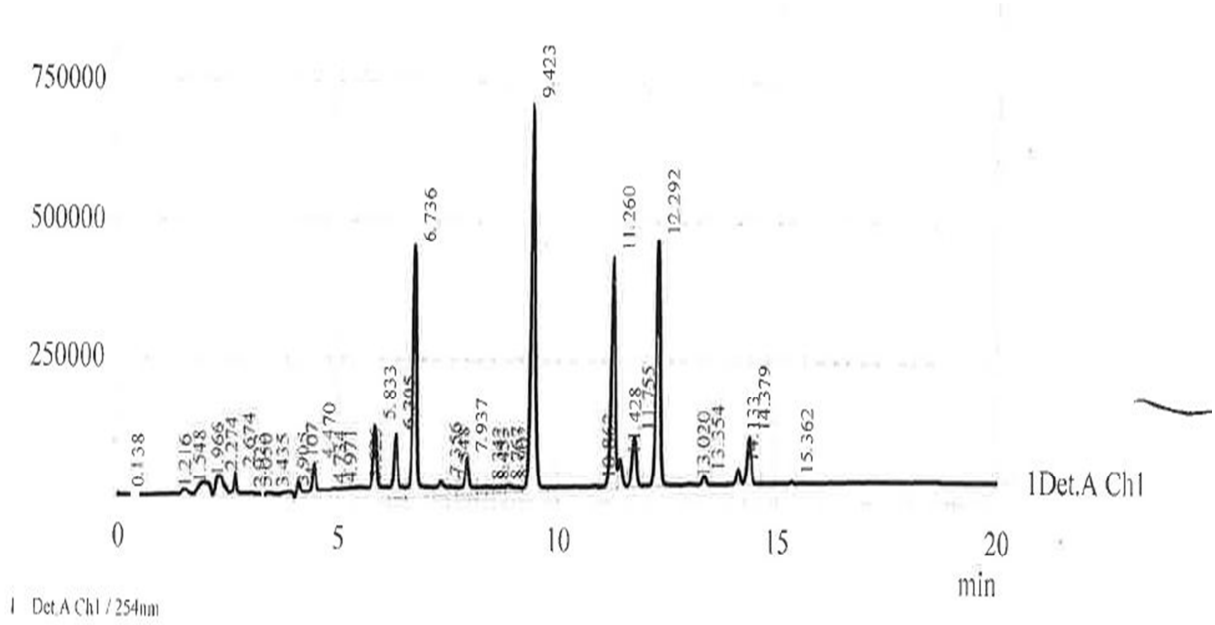

Fig (4) Chromatogram of PAHs compounds in Kurdish rice husk (north Iraq)

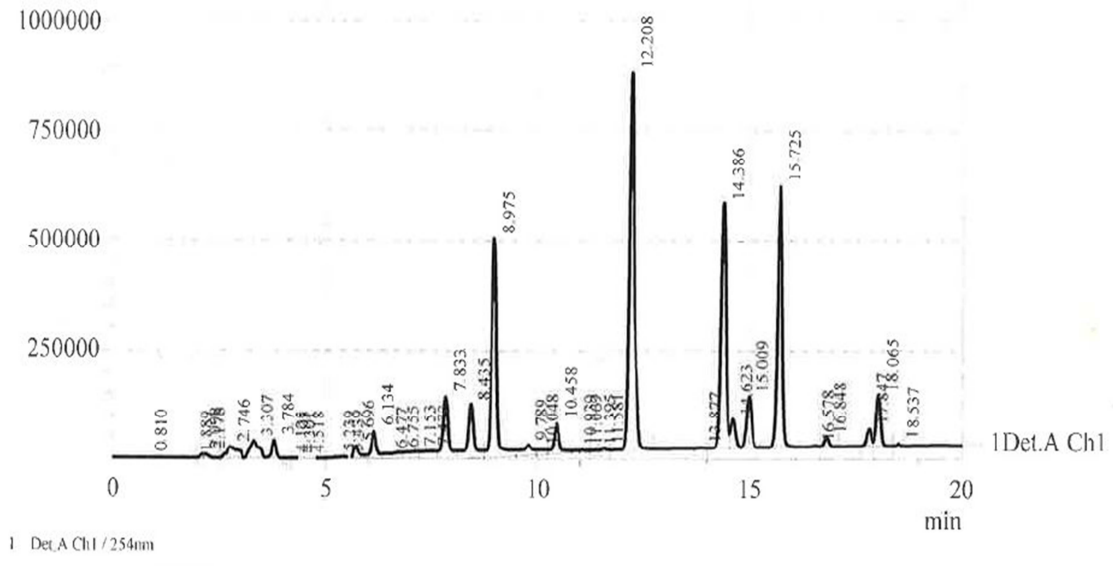

Fig (5) Chromatogram of PAHs compounds in Arabian rice husk (south Iraq)

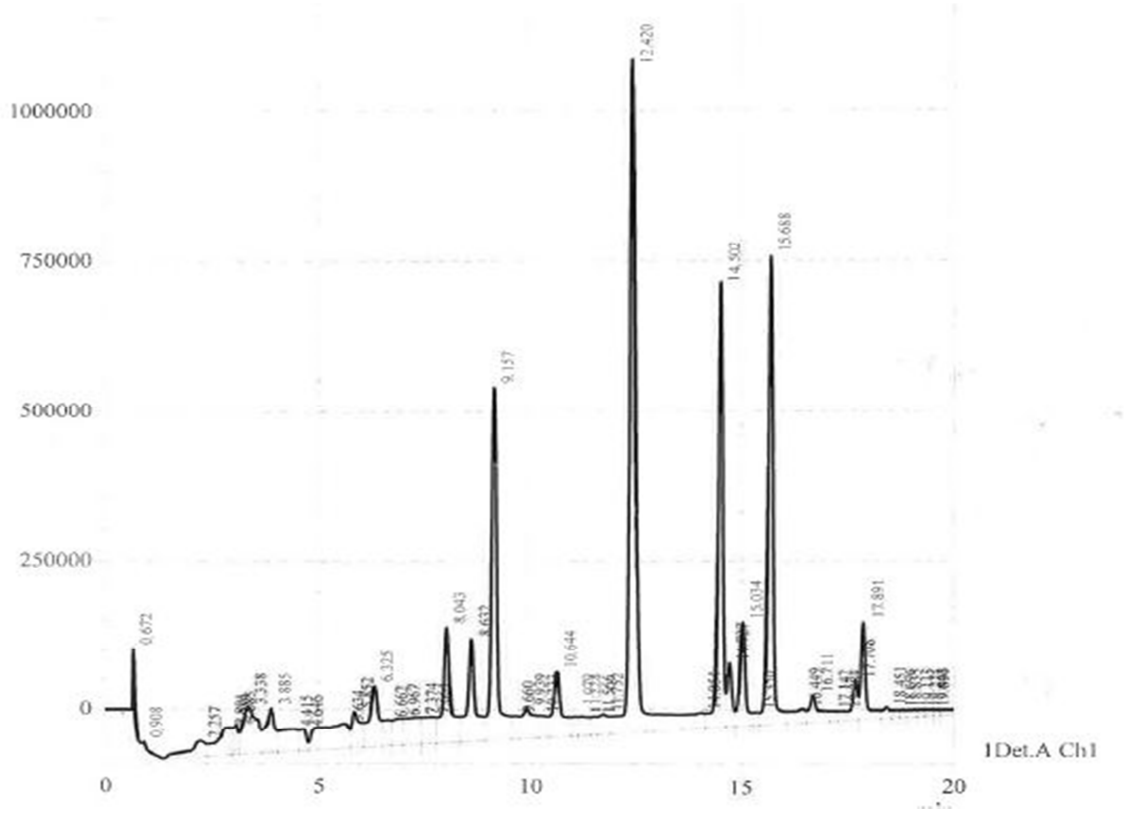

Fig (6) Chromatogram standard of PAHs compounds

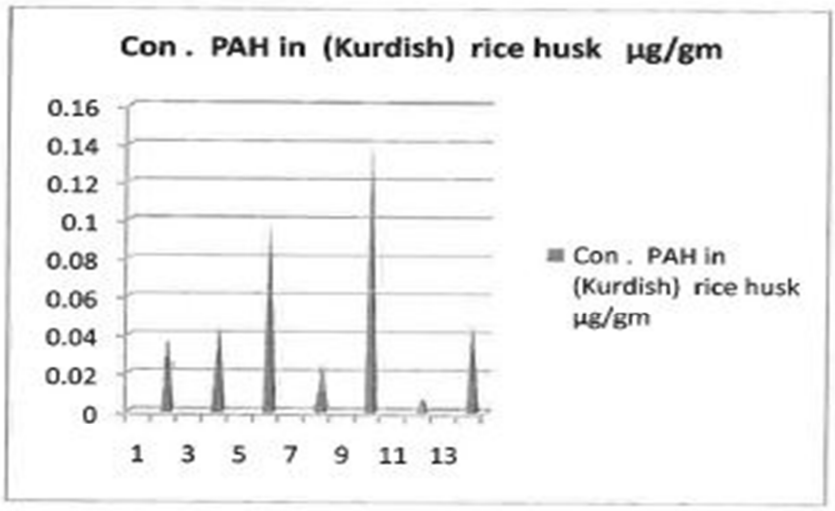

Fig (7) concentration of PAHs naphthalene, acenaphthylene, acenaphthlene,benzo(a)anthracene, benzo(k)flouanthene, benzo(g.h,i)perylene, ideno(1,2,3cd)pyrenen respectively in Kurdish rice husk µg/gm

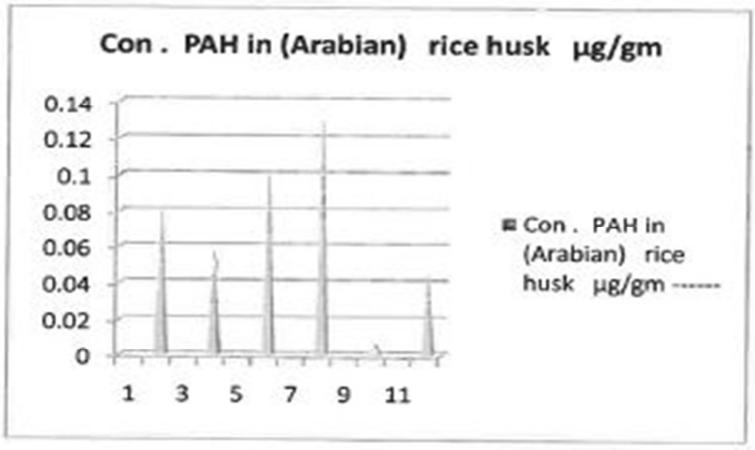

Fig (8) concentration of PAHs Acenaphthylene, acenaphthlene,benzo(a)anthracene, benzo(k)flouanthene, benzo(g.h,i)perylene, ideno(1,2,3cd)pyrenen respectively in Arabian rice husk µg/gm

Result and Discussion :

The determination of PAHs compounds as potential carcinogenic is one of the most important tasks in environmental analysis, PAHs have a dangerous impact on the environment particularly humans in some condensation. HPLC analysis of (PAHs) in two different rice husk (Kurdish Arabic) and the total PAH concentration are represented in table 1 ,from the result show that rice husk (Kurdish) contain 7 types of (PAHs) (Naphthalene, Acenaphthylene, Acenaphthlene, Benzo(a)anthracene, Benzo(k) fluoranthene, Benzo(g.h.i)perylene, ldeno(l,2,3cd)pyrene) while ,(Arabic) rice husk contain 6typesof (PAHs)(Acenaphthylene, Acenaphthlene, Benzo(a)anthracene, Benzo(k)fluoranthene, Benzo(g.h.i)perylene, ldeno(l,2,3cd)pyrene). HPLC Chromatograms of two types of rice husk for (PAHs) shown in Fig(4,5), HPLC Chromatograms of standards of (PAHs) shown in Fig(6). The structure of some of Polycyclic Aromatic Hydrocarbons(PAH) in rice husk shown in Fig (3). Fig (7) shows a concentration of different (PAHs) in Kurdish rice husk, that Benzo(k)fluoranthene has a higher concentration, but Benzo(g.h.i)perylene have a lower concentration in rice husk Fig(8) shows the density of different (PAHs) in Arabic rice husk, that also Benzo(k)fluoranthene have a higher concentration, but Benzo(g.h.i)perylene have a lower concentration in rice husk. As a carcinogen and persistent in the environment for long periods, PAHs have a dangerous impact. The most natural cause of defilement by PAHs in rice roots is irrigation water. Cereal defilement with PAHs is usually minimal but elevated intake makes nourishment the primary mode of ingestion. The collection of PAHs happens in a few structures, with prevalence for the root, taken after by the husk. Hata et al. (2014) concur with the highest accumulation of PAHs in wood and rice husk medications.analytical HPLC by using different column packings is suitable for the analysis of different samples furnishing additional or in some cases sufficient information for the identification and determination of aromatic compounds.

Conclusion:

Rice husk (RHs) as an agro-waste generated from rice production, while its application is limited. a carcinogen and diligent in the environment for long periods, PAHs have a dangerous impact. HPLC technique can be used for the prefractionation of complex samples furnishing well seperated , more simplified fractions for further analysis.The HPLC analysis was used for comparative quantitative and qualitative determination of (PAHs) in two different rice husks in Iraq country. polycyclic aromatic hydrocarbons are fairly simple compounds that are cause for concern when found in the environment. the concentration of PAHs of north rice husk is lower than in south rice husk (4.043,4.388)respectively,i.e. species higher carcinogenic than the other. This dated method could help to identify the level of numerous toxic in different rice husk., Benzo(g.h.i)perylene, indeno(l,2,3cd)pyrene have the same concentration in both types of rice

husk, Benzo(k)fluoranthene is the most abundant in both type of rice husk, while Benzo(g.h.i)perylene have a lower concentration in two rice husk's types.

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References

[1] Anthony R. Bird,Takashi Hayakawa, Yustinus Marsono, James M. Gooden,Ian R. Recorde. *"Coarse Brown Rice Increases Fecal and Large Bowel Short-Chain Fatty Acids and Starch but Lowers Calcium in the Large Bowel of Pigs*". The Journal of Nutrition. Vol. 130, No. 7, pp. 1780–1787. (2000).

[2] Ming-Hsuan Chen,Nobuyuke Kozukue,Hyun-Jeong Kim, Mendel Friedman. *"Growth-inhibitory effects of pigmented rice bran extracts and three red bran fractions against human cancer cells: relationships with composition and antioxidative activities*". Journal of Agricultural and Food Chemistry. Vol. 60, No. 36, pp. 9151-9161. (2012).

[3] Sung Phil Kim, Jun Young Yang, Mi Young Kang, Jun Cheol Park, Seok Hyun Nam, and Mendel Friedman. *"Composition of Liquid Rice Hull Smoke and Anti-Inflammatory Effects in Mice*". Journal of Agricultural and Food Chemistry. Vol. 59, No. 9, pp. 4570–4581. (2011).

[4] V. Van Hoed,G. Depaemelaere, J. Vila Ayala, P. Santiwattana, R. Verhé , and W. De Greyt. *"Influence of Chemical Refining on the Major and Minor Components of Rice Bran Oil*". JAOCS. Vol. 83, No. 4, pp. 315-321. (2006).

[5] Wells, J.H.*"Utilization of Rice Bran and Oil in Human Diets"*. Louisiana Agriculture. Vol. 36, pp. 5-8. (1993).

[6] E.A.M. de Deckere, Ph.D., and O. Korver, Ph.D. *"Minor Constituents of Rice Bran Oil as Functional Foods*". Nutrition Reviews. Vol. 54, No. 11, pp. 120- 126. (1996).

[7] David Satcher,M.D.,Ph.D. *"Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs)*". (1995).

[8] Denys Leclerc ,Wen Li Duo, Michelle Vessey. *"Effects of combustion and operating conditions on PCDD/PCDF emissions from power boilers burning salt-laden wood waste*". Chemosphere Vol. 63, pp. 676–689. (2006).

[9] Bethesda, MD. *"Hazardous Substances Data BankNational library of medicine*". National toxicology program. (1994).

[10] Benjamin A. Rybickia, Nora L. Nock , Adnan T. Savera , Deliang Tang , Andrew Rundle. *"Polycyclic aromatic hydrocarbon-DNA adduct formation in prostate carcinogenesis*". Cancer Letters. Vol. 239, pp. 157-167. (2006).

[11] Knafla A., Phillipps K.A., Brecher R.W., Petrovic, S. and Richardson M. *"Development of a dermal cancer slope factor for benzo[a]pyrene*". Regulatory Toxicology and Pharmacology. Vol. 45, pp. 159-168. (2006).

[12] K.B. Okona-Mensah, J. Battershill, A. Boobis , R. Fielder. *"An approach to investigating the importance of high potency polycyclic aromatic hydrocarbons (PAHs) in the induction of lung cancer by air pollution*". Food and Chemical Toxicology. Vol. 43, pp. 1103-1116. (2005).

[13] mastral, A. m.,Callen, mayoral,C. and Galbfin , J. *"Polycyclic aromatic hydrocarbon emissions from fluidized bed combustion of coal*". Fuel. Vol. 74, No. 12, pp. 1762-1766. (1995).

[14] Cabanas,A., Saez, F., Gonzalez,A.and Escalada,R. *"Quantitative assesssment of polycyclic aromatic hydrocarbons fro crock waste combustion emission*". Journal of Agricultural Engineering Research. Vol. 77, No. 3, pp. 349-354. (2000).

[15] J.W. Hodgeson,W.J. Bashe , T.V. Baker. *"Determination of polycyclic Aromatic Hydrocarbons in Drinking Water by Liquid –Liquid Extraction and HPLC with Coupled Ultraviolet and Fluorescence Detection"*. Technology Applications Inc. (1990).

[16] Mohammed Shahid Akhlaq. *"Polycyclic aromatic hydrocarbons in crude oil-contaminated soil: A two-step method for the isolation and characterization of PAHs*". Environmental Science and Pollution Research. Vol. 4, pp. 217–222. (1997).

[17] Stephen A. Wise, Lane C. Sander and Willie E. May. *"Determination of polycyclic aromatic hydrocarbons by liquid chromatography*". Journal of Chromatography. Vol. 642, pp. 329-349. (1993).

[18] Linda S. Johansson, Bo Leckner , Lennart Gustavsson , David Cooper, Claes Tullina , Annika Potter. *"Emission characteristic of modern and old-type residential boilers fired with wood logs and wood pellets*". Atmospheric Environment. Vol. 38, pp. 4183-4195. (2004).

[19] F. Saez , A. Cabanas, A. Gonzalez, J.M. Murillo, J.M. Martinez, J.J. Rodriguez, J.L. Dorronsoro. *"Cascade Impactor Sampling to measure Polycyclic Aromatic Hydrocarbons from Biomass Combustion Processes*". Biosystems Engineering. Vol. 86, No. 1, pp. 103–111. (2003).