DOI: http://dx.doi.org/10.21123/bsj.2021.18.1.0132

Continuous On-Line Tar Measurements for Gasification Process Monitoring using Fluorescence Excitation-Emission Matrices at Elevated Temperature

Shaimaa S Mahdi

Department of Physics, College of Science for Women, University of Baghdad
Corresponding author: shaimaa.saleh@csw.uobaghdad.edu.iq
ORCID ID: https://orcid.org/0000-0001-5204-9541

Received 16/11/2019, Accepted 15/3/2020, Published Online First 6/12/2020, Published 1/3/2021

Abstract:

Biomass has been extensively investigated, because of its presence as clean energy source. Tars and particulates formation problems are still the major challenges in development especially in the implementation of gasification technologies into nowadays energy supply systems. Laser Induced Fluorescence spectroscopy (LIF) method is incorporated for determining aromatic and Polycyclic Aromatic Hydrocarbons (PAH) produced at high temperature gasification technology. The effect of tars deposition when the gases are cooled has been highly reduced by introducing a new concept of measurement cell. The samples of PAH components have been prepared with the standard constrictions of measured PAHs by using gas chromatograph (GC). OPO laser with tuning rang of (200 to 2400) nm and peak energy of 2.2 mJ were used to excite the tar compounds, which have fluorescence properties in the range of ultraviolet| blue spectral range. The measurements have been evaluated by incorporating the Excitation-Emission Matrices (EEM), presented as time consuming method for tar monitoring.

Key words: Biomass, EEM matrix, Laser Induced Fluoresces (LIF), PAH compounds, Renewable energy

Introduction:

Owing to the world population increase, which leads to rising the energy consuming and prices. Gasification of biomass is presented as an alternative solution for the dependency on the fuels (1,2). One of the main issues associated with biomass gasification is how Tars can be defined. Tar presents the mixture of chemical compounds which condense at low temperature and have boiling point higher than 150℃ (3). While, Tar formation is undesirable according to the problems associated with its condensation and polymerization to form more complex structures, which causes problems in the process equipment used in the application of the produced biogas. Tar measurement and characterization are required for efficient biomass gasification. Aromatic and Polycyclic Aromatic Hydrocarbons (PAH) are produced in high temperature thermochemical conversion processes leading to delicate the quality of bio-gases (3,4). Because this process step is especially connected in the field of biomass conversion with significant effort and high specific costs, a new and cost-effective method for tar conversion or tar separation has been intensively investigated (5,6). So many researchers have paid attention to find the appropriate solutions for these obstacles starting with offline European detection methods. Because these offline methods are time-consuming and the nature of PAH which creates problems in the offline systems as mentioned above, some other methods have used the online quantitative and qualitative detection measurements like photo ionization detection, laser induces fluorescence LIF, (IR) Absorption, FTIR, and Raman spectroscopy (7, 8). A big drawback is the analyzability success of these measures. An easy to handle on-line monitoring system of gas phase is explored for years, but so far it is only imperfectly realized in the academic field. A compelling, robust measurement and monitoring system is not available yet (9).

In this work, the measurements have been carried out at the Technical University of Berlin (Institute for Energy Technology). Basic scientific studies of the possibilities of fluorescence spectroscopy for the analysis of organic component are carried out in the hot process gases by means of laser induced fluorescence (LIF). Generally, spectroscopy is an analytical method which can be achieved from the interaction of species with electromagnetic radiation.

In Laser Induced Fluorescence (LIF) Spectroscopy, the molecules are absorbing photons of the incident light. After absorbing the energy and reaching one of the higher vibrational levels of an excited state, these molecules are going to fall to the lowest vibrational level of the excited state, when it loses its excess of vibrational energy by collision. The molecules then go through internal conversion, influenced by vibrational relaxation and heat dissipation to the environment. As the excited molecules return to the ground state, they are emitting photons in the form of fluorescence corresponding to a longer wavelength than the absorbed photon. The induced fluorescence characteristic for the concentration and temperature of the interested molecules and generally all data are presented as emission spectra by plotting the fluorescence intensity and emission wavelengths.

Through the alternating use of different wavelengths, detailed information on the composition of the Tar forming substances can be recovered in the product gas. Motivations are to refine the methods to develop appropriate measurement setups, identify limitations and develop evaluation methods. In this paper (LIF) is the method incorporated to develop a Tar sensor to minimize the formation of PAHs in the high temperature combustion system. The aim of this work is to describe the innovation of on-line optical method for determining aromatic and Polycyclic Aromatic Hydrocarbons (PAH) produced at high temperature gasification technology. Also, it focused on the development of technology of gasification processes reliable, robust and fast measurement systems. For the analysis of the produced gases that are indispensable, a sensor, that continuously provides detailed information on the loading of the product gas with aromatics, could give a decisive boost, continuous process monitoring and control. The measurement methods for the analysis of Tar in gasification processes with an emphasis on the usage of biomass also have been investigated in this research work. The final overall goal is to develop a robust process sensor and being able to control such on-line Tar-Monitoring system to use it in an industrial demonstration projects.

Materials and Method:

An Optical Parametric Oscillator laser OPO (Opolette, Fa. OPOTEC Inc) was used to detect the Fluorescence of PAHs with tunable range of (200 to 2400) nm. The laser has pulse width of 7 ns, a repetition rate of 20 Hz, peak energy of 2.2 mJ, and beam diameter of 5 mm. Figure 1 shows the scheme of the experimental setup used for performing the measurements. Emission has been focused using a set of UV-enhanced mirrors. A beam splitter was placed after the mirrors, where 70% from laser power to excite the hot gases and 30% to measure the laser power.

The measuring cell has been designed into a spherical geometrical design to ensure an efficient light collecting generated by the fluorescence process. The measurement cell has windows with a hot N_2 washing concept to reduce the effect of condensable hydrocarbons with increasing the temperature. Multi-mode fiber (ocean optics) has been used to collect the emitted light, which is placed perpendicular to the cell. Fluorescence measurements were performed using a Spectrograph (Andor Shamrock 303i). This spectrometer has an ICCD camera of (Andor IStar 320T), which was used to detect the resultant Fluorescence. The detection was performed with a gate width of 50 ns started when the photons of the laser are emitted. Specifically, the excitation wavelengths were scanned in 5 nm steps from 225 nm to (300 or to 315) nm. For easy viewing results and reliable efficient measurements, all instruments involved in our setup are controlled by their software's and linked to LabVIEW software.

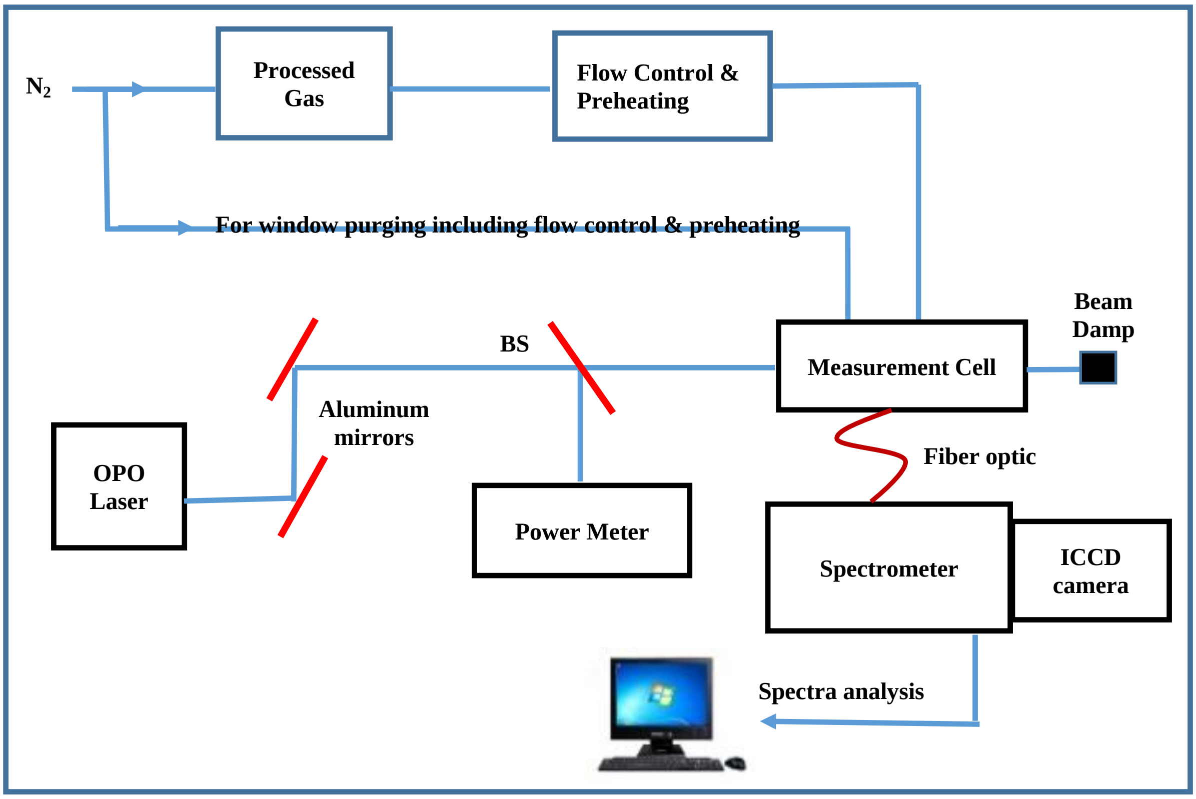

Figure 1. The Scheme of the Lab setup for the investigation of PAH compounds.

(Anth. 211.5 mg|Nm^3). The concentrations of Tar that have been considered in the procedure of samples preparation were measured by GC for real product gases from on-line gasification process. All measurements are performed at a temperature of 350°C.

Results and Discussion:

Laser induced Fluorescence spectroscopy is well known, sensitive and easily adaptable to the measurements field, but at the same time, fluorescence spectra are broad therefore, they have qualitative limitation. Thus, two- dimension Excitation-Emission Maps are considered as an efficient method to analyze the collected measurements from the spectrometer (10,11). If the individual spectra produced are assembled, 2 or 3-dimensional excitation emission matrices EEM can be generated. According to these measurements and results, the excitation wavelengths to reach the highest Fluorescence intensity of the PAH components were figured out.

Specifically, the Gas chromatography GC is commonly used for offline analysis and measurement of PAH compounds by using a flow-through narrow tube, where different gas samples pass with the help of a carrier gas in order to be analyzed. GC provides both qualitative and quantitative analysis also for complex mixtures. To develop online tar measurements in our research, the concentration of our prepared samples depended on the GC analyzed results. The tested gases have been prepared by using a test gas setup, which includes PAH compounds dissolved into Toluene and syringe pump to provide the test gas. The tested gas was carried by hot N_2 and controlled by a mass flow controller. This setup was very stable to provide PAH compounds in gas phase. The PAHs compound considered to conduct our study has different numbers of rings like Benzene (Ben. 17520 mg|Nm^3), Naphthalene (Naph. 3000 mg|Nm^3), Phenanthrene (Phen. 1000 mg|Nm^3), Fluorene (Flu. 187.5 mg|Nm^3), Acenaphthylene Ace. (1448 mg|Nm^3), Dibenzofuran (Dib. 99 mg|Nm^3), Pyrene (Pyr. 2800 mg|Nm^3) Anthracene

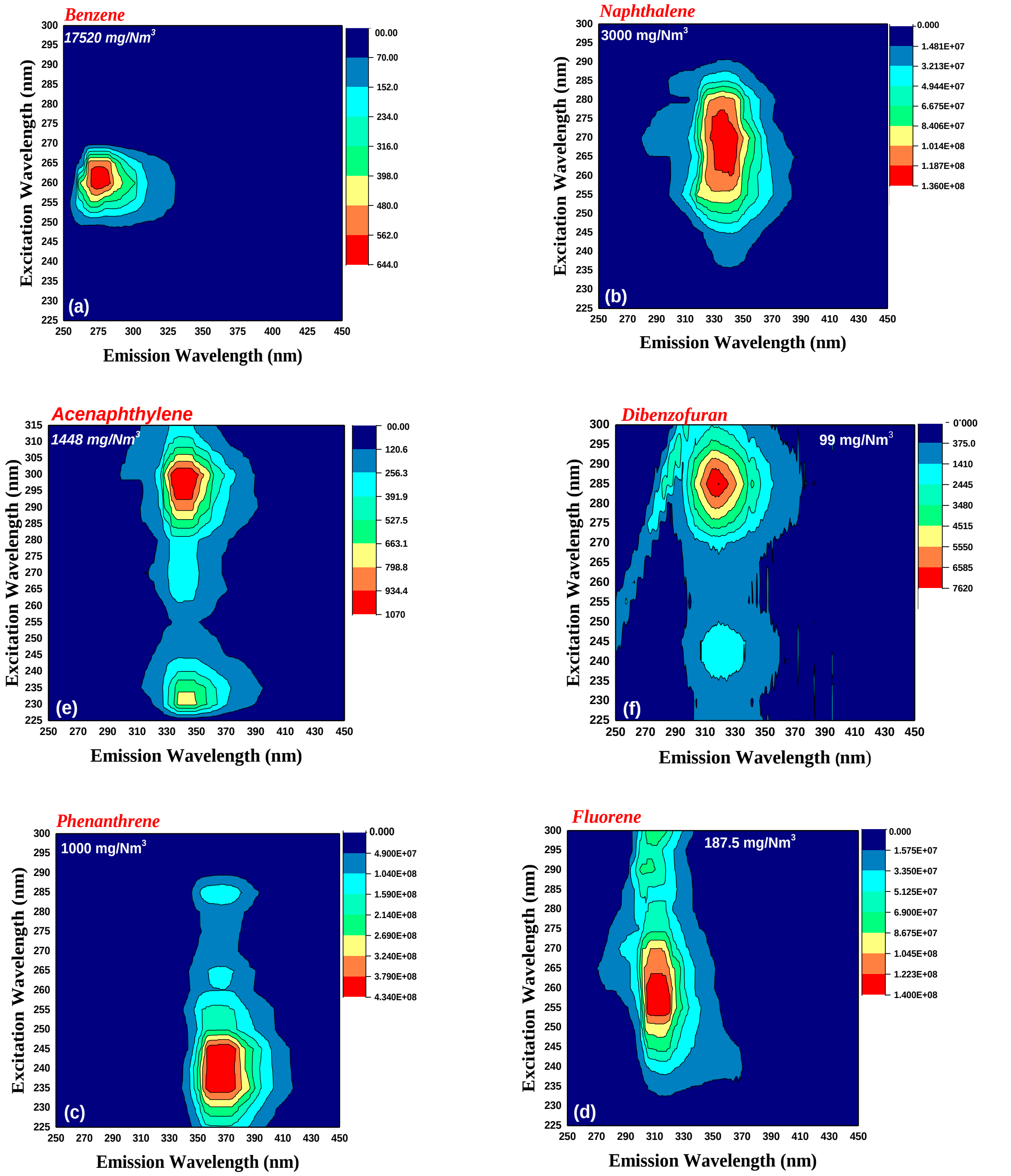

Figure 2. Excitation-Emission matrices of 6 components of PAHs at typical constrictions of a biomass gasifier, emission wavelengths are in the range of (260 – 380) nm, (a) Benzene, (b) Naphthalene, (c) Phenanthrene, (d) Fluorene, (e) Acenaphthylene, (f) Dibenzofuran.

Figuring out the effective excitation wavelengths to excite the PAHs is important to determine the wavelengths needed to develop an effective Tar sensor based on UV-light for gas cleaning in gasification process. Eight components of PAHs have been chosen in our measurements as mentioned above. A software has been programed to analyze the collected data to EEM maps, which later can be connected to the real reactor offering fast feedback about the peak fingerprint location intensity| wavelength of each output compound. By varying the excitation photons to collect the resultant intensity, each row in the EEM is an emission spectrum at excitation wavelength. On the other hand, each column in the EEM is an excitation spectrum at emission wavelength.

Figure 2 shows the EEM for the single compound of PAHs where aromatic compound with single ring can be excited in the range of deep UV (12) like Benzene as shown in Fig. 2a, benzene emits fluorescence also in the range of UV. PAHs compounds with higher rings like Naphthalene emit

Fluorescence in the range (300 to 390) nm (Fig. 2b), the highest excitation wavelength (λ_{Ex}) of Naphthalene is 266 nm (13). While λ_{Ex} of Phenanthrene is 240 nm, Flourene has λ_{Ex} of 260 and emission wavelength (λ_{Em}) of 320 nm (14) as shown in Figs. 2c and 2d, respectively. Acenaphthylene shows fluorescence at λ_{Ex} up to 290 nm to 300 nm (15) as shown in Fig. 2e. Dibenzofuran has no strong fluorescence as clear in Fig. 2f in the whole range of excitation wavelengths.

Pyrene and Anthracene excite at highest λ_{Ex} of about 235 nm and emit at λ_{Em} in the range of about (360 to 450) nm as shown in Figs. 3a, 3b, respectively.

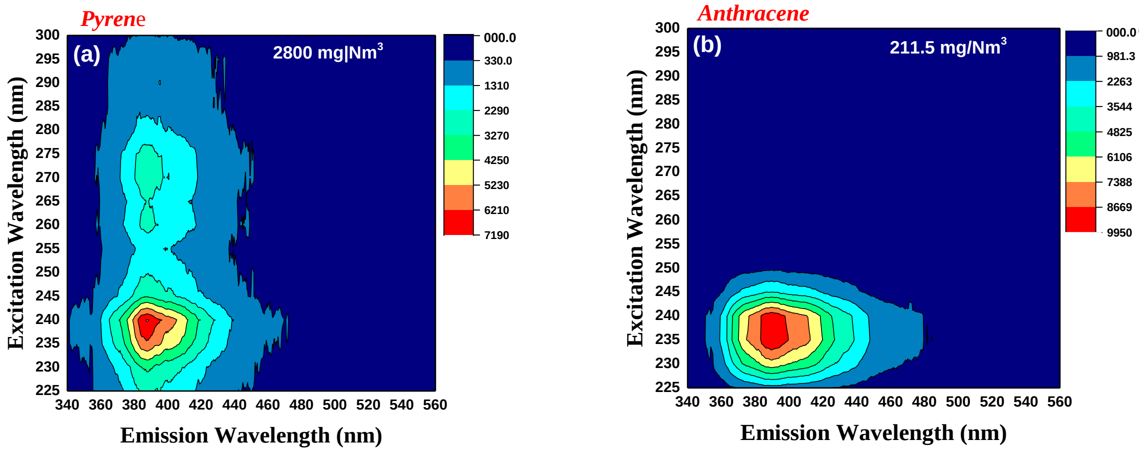

Figure 3. Excitation-Emission matrices of 2 PAH components at typical constrictions of a biomass gasifier, emission wavelengths are in the range of about (360 - 450) nm, (a) Pyrene, (b) Anthracene.

Some of PAHs compounds exhibit two peaks of fluorescence like Phenanthrene, Flourene, Acenaphthylene, Dibenzofuran, Pyrene (16) as shown in Figs. 2c, 2d, 2e, 2f and 3a, respectively. The demonstrated EEM maps are presented as references to the next step of applying our sensor for online measurement of biogas generated in the power station.

Naphthalene has two rings and presented as dominant compound results through gasification processes in the reactor (12), therefore threshold power to excite was measured to have information not only about the excitation wavelengths, but also the lowest power required to obtain fluorescence emission (17, 18). Naphthalene has high absorption peak at a wavelength of 266 nm, and thus was excited with this wavelength at various excitation powers as shown in Fig. 4. The excitation powers were reduced from 5.7 mW until 0.44 mW, and Naph. Fluorescence signal was still detectable. Therefore, the measurements of excitation threshold power show that just few sub milliwatts are enough to detect a signal of fluorescence, this result is important in the field of constriction of robust biogas sensor by replacing the OPO laser to light sources like UV LEDs.

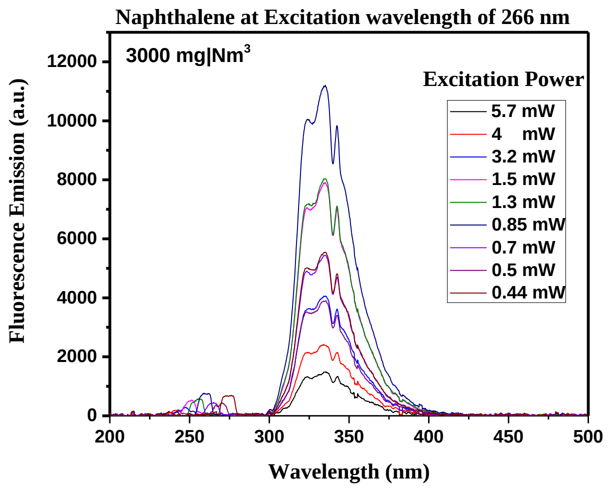

Figure 4. The required threshold power to excite Naphthalene at hot point of 350℃.

Conclusion:

The gasification process and the use of biomass gases as a renewable source of energy is a promising technology for the production of biofuels in addition to the generation of electricity and heat. The concurrent problem with biomass gasification is the production of undesirable tars, which can cause many problems in the production of energy and fuels. In order to verify the suitability of the producer gas for its further usage, Tar content must be determined. Therefore, the online optical sensor based on laser induced fluorescence is developed by improving the concept of the measuring cell and the

software used for results analyzing. This offers not only the quantification but also the qualification of gas phase Tar compounds with only optical intervention in the measured producer gas. In addition, online scanning with wavelength variance provides the ability to measure a mixture of Tars with high efficiency and short time consumption. They can be used for the continuous monitoring of gasifier tars. The obtained results show a very good match to other measurement techniques (7, 10), but in our work the combination of LIF technique and EEM analysis method have been developed by a new constructed design as robust instrumentation.
Experimentally, the approach of fluorescence spectroscopy of aromatics is followed in the hot process gas. Large polycyclic aromatics having three or more rings can be excited with wavelengths > 400 nm, while mononuclear aromatics such as benzene or toluene show only in the deep UV fluorescence at wavelengths in the visible light. In the near future, the integration in process control or regulation the objective pursued is planned.

Acknowledgment:

I would like to express my profound gratitude to the institute of renewable energy in the technical University of Berlin for the opportunity to work in the laboratories and support.

Author's declaration:

- Conflicts of Interest: None.
- I hereby confirm that all the Figures and Tables in the manuscript are mine. Besides, the Figures and images, which are not mine, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

References:

1. Prashant K, Zakir Kh, Michael G, Jon McC, Iain D, Ian W. Robust instrumentation and control systems for gasification of biomass. 26th Eur. Biomass Conf. and Exh. May 2018; 14-17.
2. Ahlam MF, Rasha AJ, Nafeesa JK, Wesen AM, Atheer AM. Synthesis of Silver Nanoparticles from *Malva parviflora* Extract and Effect on Ecto-5'-Nucleotidase(5'-NT), ADA and AMPDA Enzymes in Sera of Patients with Arthrosclerosis. Baghdad Sci. J. 2017;14(4):742-746.
3. Sun RZ, York N, Cardenaz-Chavez C, Behrendt F. Analysis of gas-phase polycyclic aromatic hydrocarbon mixtures by laser-induced fluorescence. Opt. Laser Eng. 2010 ;48: 1231 – 1237.
4. Christoph B, Sotirios K. Tar analysis from gasification by means of online fluorescence spectroscopy. Opt. Laser Eng. 2011; 49(7): 885-891.
5. Nicolas F, Marc T, Catherine G, Stéphane M, Roland R, Madeleine G. Identification and quantification of known polycyclic aromatic hydrocarbons and pesticides in complex mixtures using fluorescence excitation–emission matrices and parallel factor analysis. Chemosphere. 2014;107:344–353.
6. Jan N, Petr B, Sergej S, Jaroslav F, Jan K, Vaclav P. Problems related to gasification of biomass-properties of solid pollutants in raw gas. Energies. 2019;12(963):1-14.
7. Borkowski MM. Online analysis of the tar content of biomass gasification producer gas. PhD [dissertation]. Germany: Technische Universitaet Muenchen ; 2011.
8. Amanda CS, Licarion P, Adriano AG, Mario CUA. Green Chemistry method based on PARAFAC EEM data modeling for Benzo[a]Pyrene Quantitation in Distilled spirit. J Braz Chem Soc. 2019; 30:1- 2.
9. Emmanuel YK. Effect of Furnace Temperature on the Distribution of Tar during gasification of Miscanthus. J. En R R. 2018; 2(1): 1-7.
10. Michelle LN, Karl SB. Excitation-emission matrix fluorescence spectroscopy in conjunction with multiway analysis for PAH detection in complex matrices. Analyst. 2006 ;131: 1308–1311.
11. Meena KY, Rupak A, Michael DSh, Christopher PS. Fluorescence Excitation-Emission Spectroscopy: An Analytical Technique to monitor Drugs of addiction in wastewater. Water. 2019 ;11(377):1-11.
12. Iain SB, Clemens F K. Diode Laser Induced Fluorescence for Gas-Phase Diagnostics. Z Phys Chem, 2011; 225:1343–1366.
13. Orain M, Baranger P, Rossow B, Grisch F. Fluorescence spectroscopy of naphthalene at high temperatures and pressures: implications for fuel-concentration measurements. Appl Phys B. 2011; 102: 163–172.
14. Gedinger A, Spoeri R, Scheffknecht G. Comparison measurements of tar content in gasification systems between an online method and the tar protocol. Biomass Bioenerg. 2011; 111: 301-307.
15. Anunay S, Chelladurai D, Richard WF. Picosecond Time-Resolved Absorption and Emission Studies of the Singlet Excited States of Acenaphthylene. J Phys Chem. 1990; 94(18): 7106-7110.
16. Dan G, Mohit P, Kent OD, Jan BCP. Online measurements of alkali and heavy tar components in biomass gasification. Energy fuel. 2017; 31(8): 8152-8161.
17. Defoort F, Thiery S, Ravel S. A promising new on-line method of tar quantification by mass spectrometry during steam gasification of biomass. Biomass Bioenerg. 2014; 65: 64-71.
18. Jinlan X, Wenchao X, Yue-xiao Sh, Jihua T, Shuai L, Yanfen W, et al. Excitation-emission matrix (EEM) fluorescence spectroscopy for characterization of organic matter in membrane bioreactors: Principles, methods and applications. FESE. 2020; https://doi.org/10.1007/s11783-019-1210-8.

القياسات المستمرة والفورية لمركبات القطران (Tar) الناتجة عن عملية التغويز (حرق الخشب) ومراقبتها بأستخدام مصفوفات ألإثارة-الأنبعاثات عند درجات الحرارة العالية

شيماء صالح مهدي

قسم الفيزياء، كلية العلوم للبنات، جامعه بغداد، بغداد ، العراق.

الخلاصة:

تم التحقيق والكشف في المواد او المخلفات الحيوية على نطاق واسع كونها تعتبر مصدر من مصادر الطاقة النظيفة. لكن مع هذا بقيت مشاكل تكوين القطران والجسيمات من اهم المعوقات في التنمية وخاصة في مجالات تطبيق التغويز في انظمة الامداد بالطاقة و لغاية يومنا الحاضر. ان الهدف من هذا البحث هو وصف لابتكار طريقة بصرية تعطي نتائج مباشرة عبر الانترنيت لحساب المركبات العطرية والمركبات الهيدروكاربونية المتعددة الحلقات PAH والناتجة بسبب تقنيات التغويز عند درجات الحرارة العالية وذلك عن طريق استخدام التحليل الطيفي للفلورة المستحثة بالليزر. تم تقليل ترسب القطران المتكون عند تبريد الغازات من خلال ادخال مفهوم جديد في تصميم وحدات او الاجزاء الخاصة بالقياس . تم تحضير عينات مركبات ال PAH باستخدام المعايير القياسية لمركبات ال PAHs المقاسة وذلك بأستخدام كروموتوغرافيا الغازات GC، حيث تم استخدام ليزر نوع OPO بمدى ضبط يتراوح من 200 إلى 2400 نانومتر و ذروة طاقة قدرة 2,2 ملي جول لإثارة مركبات القطران والتي لها خصائص فلورة في مدى النطاق الطيفي الفوق بنفسجي. تم تقييم القياسات من خلال دمج مصفوفات الإثارة-الانبعاثات (EEM)، والتي تعتبر كطريقة لتقليل استهلاك الزمن الازم لرصد القطران.

الكلمات المفتاحية: الغازات الحيوية، مصفوفات تحفيز- أنبعاث، الفلورة المحتثة بالليزر، المركبات الاروماتية، الطاقة البديلة.