A Laser induced fluorescence design for renewable energy application

Shaimaa S. Mahdi
University of Baghdad| college of science for women|physics department, shaimaa.saleh@CSW.uobaghdad.edu.iq

Intisar A. Hamad
university of Baghdad| college of science for women| physics department, intisarah_phys@csw.uobaghdad.edu.iq

University of Kerbala

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Abstract

Biomass is considered to be one of the highest potential renewable energy sources to meet the requirements of energy in the world, where it can be used as an effective alternative for renewable energy sources, including electricity and heating, as well as fuel used in transport. One of the most common problems accompanying the usage of biomass through gasification processes to produce gases is the amounts of undesirable formed Tars. In this paper, a Laser Induced Fluorescence spectroscopy (LIF) method was incorporated to identify the produced Tar compounds at high temperature in the gasification technology. The effect of tars deposition when gases are cooled was greatly reduced by introducing a new concept of the measurement cell. The processed mixtures of Tar samples were prepared with the standard constrictions of measured aromatic and Polycyclic Aromatic Hydrocarbons (PAHs) by using Gas Chromatograph (GC). Optical Parametric Oscillator (OPO) laser with a tuning range of (200 to 2400) nm and peak energy of 2.2 mJ was used to excite the Tar compounds, which have fluorescence properties in the range of ultraviolet|blue spectrum. The investigated measurements were evaluated by incorporating the Excitation-Emission Matrices (EEM), which was presented as a time-consuming method of online Tar monitoring.

Keywords

Biomass, EEM matrix, Laser induced fluoresces (LIF), PAH compounds, Renewable energy

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Cover Page Footnote

1. Introduction

Biomass gasification technique has gained significant attention since the last 30 years [1], where it utilizes biomaterials derived from plants and trees as a source of energy by the thermal decomposition process which in turn produces a normal mixture of gases (Nitrogen, Hydrogen, Carbon dioxide, Methane, etc.) that can be used in the advanced applications like gas engine fuel [1,2]. The main component of the gasifier system is the reactor where gasses are generated, in addition to a series of cooling and purification systems that cool and purify the product gasses [3]. In the gasification technique, the most hindered progression is in the Tar formation and the expensive methods for removing those complex components [4]. So many researchers have paid attention to find the appropriate solutions for these challenges starting with the offline European detection methods. The long time-consuming in those offline methods adding to the interact nature of the Tar mixture like structures and the variation of polarity, lead to the re-polymerization of samples with time [4−6]. To avoid these problems in the offline systems, some methods have used the online quantitative and qualitative detection measurements like photo ionization detection, laser induces fluorescence LIF, and LED induced fluorescence [7−10].

Tar presents the mixture of chemical compounds which condense at low temperature and have boiling point higher than 150 C [11]. The point of departure for this work is the undesirable effect of Tar formation and the problems associated with its condensation and polymerization to form more complex structures which cause problems in the process equipment used in the application of the produced gas. That is, the objective of this research is to design and build an integrated system based on laser-induced fluorescence, gas chromatography (GC) and develop a robust process sensor to provide online analysis of the producer gasses and thus it will be easy to control the gasification parameters like air, steam, etc. Moreover, to develop the analytical method in determining the Tar compounds and overall quantity.

2. Materials and methods

Tar measurement and characterization are required for efficient biomass gasification. The mixture of Tar produced through the gasification process needs to be well measured and analyzed. In our lab, the mixture of Tar compounds was investigated by incorporating LIF presented as an attractive optical technique with the possibility of online measurements and analyzing the Tar content in this process.

The calibration of the optical measurement technique has been designed for the detection of fluorescence signals that are emitted from the Tar compounds of our investigation. The optical and prepared Tar mixing setups were directly coupled through a heated tube to avoid the gas phase PAHs condensation.

The optical setup is shown in Fig. 1. An OPO laser (Opolette, Fa. OPOTEC Inc) was used to detect the Fluorescence of PAHs with a tunable range of (200−2400) nm. The laser has a pulse width of 7 ns, a repletion rate of 20 Hz, peak energy of 2.2 mJ, and a beam diameter of 5 mm. Laser emission was focused on using a set of UV-enhanced mirrors. A beam splitter was placed after the mirrors, where 70% of laser power was to excite the hot gases and 30% to measure the laser power. A power meter constantly monitors the illuminated power which reaches the cell. A measurement cell was designed in a geometric shape hollow cylinder as shown in Fig. 1, which ensures collecting generated photons as much as possible by the fluorescence process.

The measurement cell has windows with hot N_2 as a washing concept to reduce the effect of condensable hydrocarbons with increasing the temperature. Multimode fiber (ocean optics) has been used to collect the emitted light. Fluorescence measurements were performed using a Spectrograph (Andor Shamrock 303i). This spectrometer has an ICCD camera (Andor IStar 320T), which was used to detect the Fluorescence. The emission spectra have been detected perpendicularly to excitation with special multi-mode fiber optics. The detection was carried out with a gate width of 50 ns started when the laser photons were emitted.

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 aid of carrier gas in order to be analyzed. The quantitative and qualitative analysis for the complex mixtures was also conducted by the Gas chromatography. To develop online tar measurements in our research, the concentration of our prepared samples was depending on the GC analyzed results. The tested gases have been
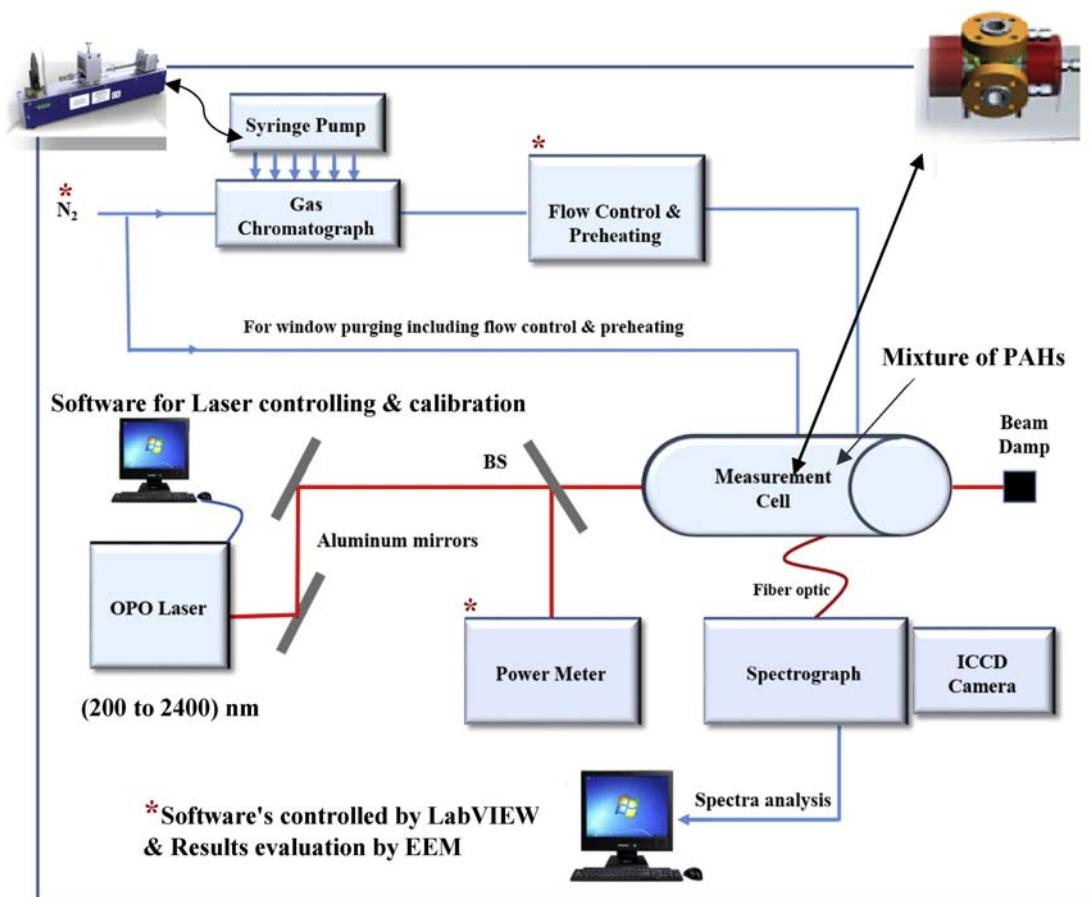
Fig. 1. The experimental setup used for performing the optical measurements technique.

prepared by using a test gas setup including polycyclic aromatic hydrocarbon PAH (Tars) 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 a gas phase. The four PAHs compounds considered to conduct our study are known in biomass gasification and have different numbers of rings like Naphthalene (Naph. 3000 mg|Nm^3), Phenanthrene (Phen. 1000 mg|Nm^3), Fluorene (Flu. 300 mg|Nm^3), Pyrene (Pyr. 560 mg|Nm^3). The concentrations of Tar that have been considered in the procedure of sample preparation were measured by GC for real product gases from the on-line gasification process. To prevent the occurrence of tar compounds condensation, the measurement cell was heated electrically to 350 C. The data acquisition and analysis of the experimental results were controlled by connecting all software devices in a computer through LabVIEW, allowing for efficient data collecting and direct analysis.

3. Results and discussion

In spite of the fact that Laser-induced Fluorescence spectroscopy is well known, sensitive, and easily adaptable to the measurements field, yet at the same time, fluorescence spectra are broad. So, they have qualitative limitations (spectral overlapping between absorption and emission spectra). Therefore, two-dimension Excitation-Emission Maps are considered as an efficient method to analyze the collected measurements from the spectrometer [12−14]. The software has been programmed to analyze the collected data. Four components of PAHs have been chosen in our work. Depending on the classification suggested by van Paasen et al. [15], the measured PAHs are related to classes 3 and 4.

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 the gasification process. The software has been programmed to analyze the
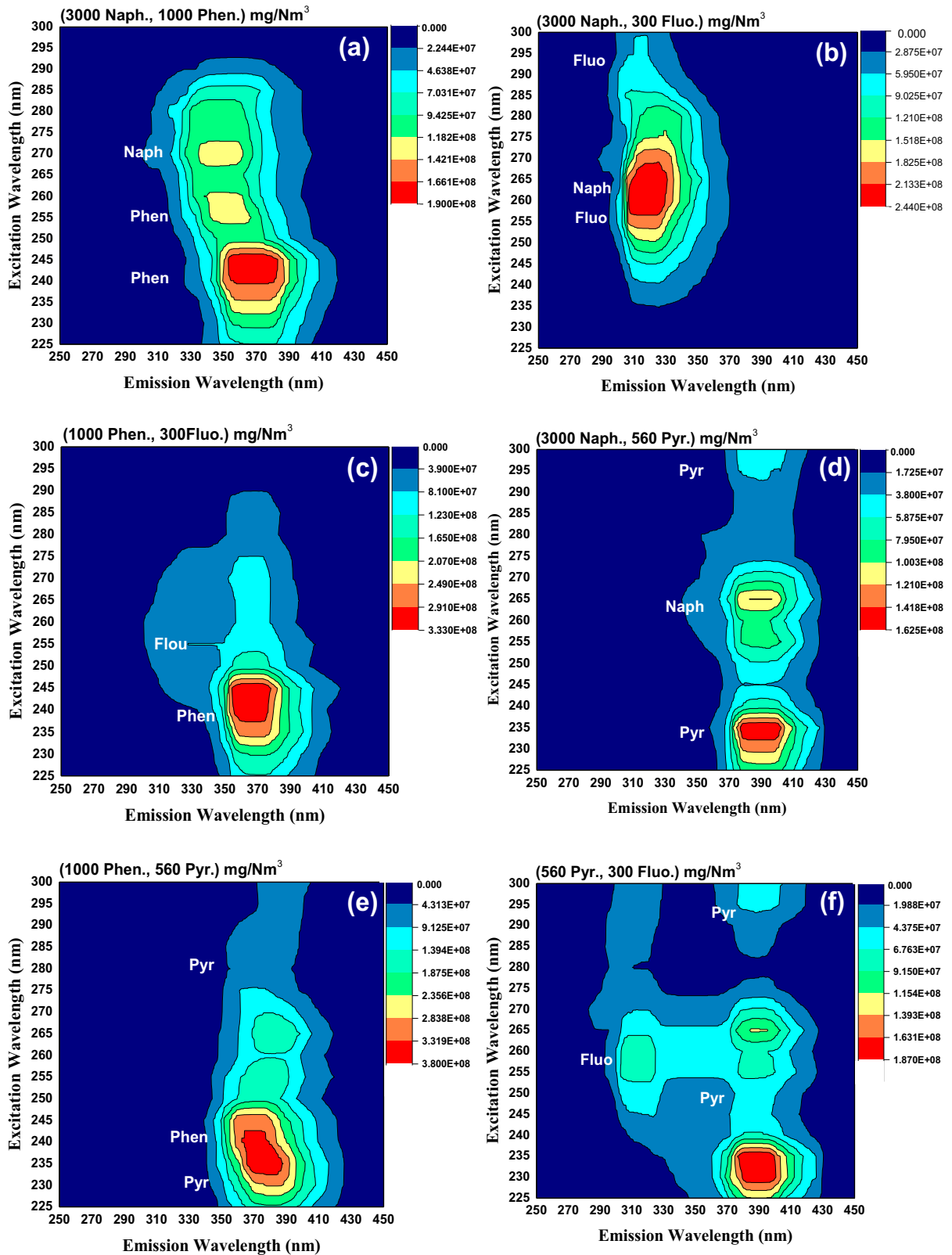
Fig. 2. Excitation-Emission matrices of a mix of PAHs (Naph. 3000 mg|Nm^3, Phen. 1000 mg|Nm^3, Flu. 300 mg|Nm^3, Pyr. 560 mg|Nm^3) components at typical constrictions of a biomass gasifier, scanning excitation wavelengths are in the range of (225—300) nm, a) Naph. & Phen., b) Fluo. & Naph., c) Phen. & Fluo., d) Naph. & Pyr., e) Phen. & Pyr., f) Fluo. & Pyr.

collected data to EEM maps, which can later be connected to the real reactor offering fast feedback about the peak fingerprint location intensity wavelength of mixed output Tar compounds. By varying the excitation photons to collect the resultant intensity, each row in the EEM is an emission spectrum at the excitation wavelength. On the other hand, each column in the EEM is an excitation spectrum at the emission wavelength. Fig. 2 shows the EEM contour maps for the mixture of PAHs compound, where the EEM

fingerprint is agreed with EEM for each separated compound as shown in previous studies [1,16,17]. The range of the emission and excitation wavelengths of the selected Tar mix labeled in Fig. 2 are determined according to the EEM for each single PAH compound in our previous research [16]. Naphthalene has two rings, while Phenanthrene has three rings. Therefore, Phenanthrene gives a fluorescence stronger than Naphthalene as shown in Fig. 2a. Fluorene and Naphthalene have a similar number of rings and show
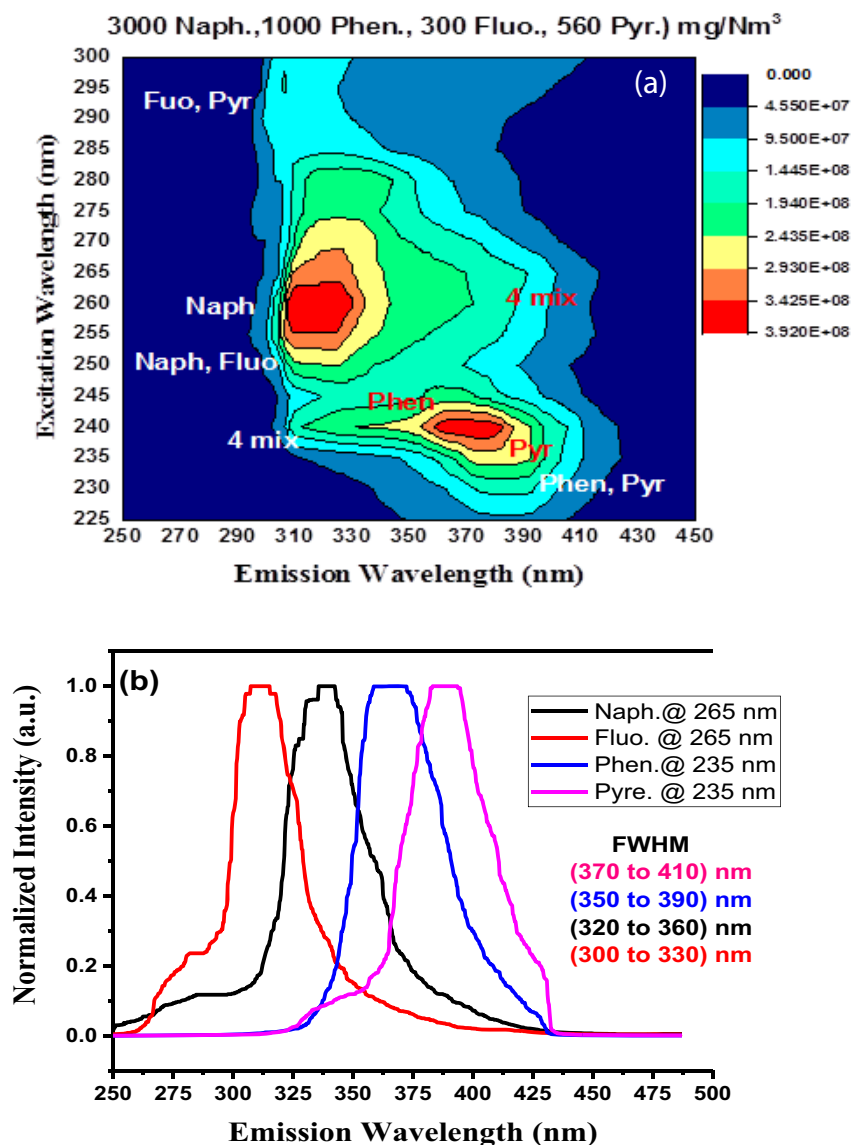

Fig. 3. **a**. Excitation-Emission matrices of four PAHs mixture (Naph. 3000 mg|Nm³, Phen. 1000 mg|Nm³, Flu. 300 mg|Nm³, Pyr. 560 mg|Nm³) components at typical constrictions of a biomass gasifier, scanning excitation wavelengths are in the range of (225−300) nm, **b.** Fluorescence emission spectra corresponding to PAHs in (a).

high fluorescent in the range of (300–360) nm, but Fluorene excitation wavelengths extended to nearly 300 nm as shown in Fig. 2b. For the same reason mentioned above, Phenanthrene shows strong fluorescence in the range of (350–390) nm centered at 370 nm, compared with Fluorene which has weak fluorescence in the range of about (310–350) nm as shown in Fig. 2c. In Fig. 2d, Pyrene has four rings and absorbs most of the excitation energy, therefore Naphthalene appears very week in comparison with Pyrene. The EEM fingerprint shown in Fig. 2e has an emission range in between (350–410) nm, this range leads to the fluorescence emission range of Pyrene (370–410 centered at 390) nm and Phenanthrene. The EEM shown in Fig. 2f is significantly separated into two ranges corresponding to Fluorene and Pyrene.

Fig. 3a shows the EEM fingerprint of four PAHs incorporated in this investigation, and 3b shows the related fluorescence emission spectra. The full width at half maximum (FWHM) range of each compound as follows: Naph. (320–360) nm, Fluo. (300–330) nm, Phen. (350–390) nm, Pyre. (370–410) nm corresponding to about 30–40 nm, which agrees with [17].

By comparing a, b in Fig. 3, it is found to be that there is a good matching between the fingerprint map and the fluorescence spectra from the start, end, and emission wavelengths. On the other hand, the excitation wavelengths chosen in Fig. 3b are according to the highest fluorescence emission shown in Fig. 3a. For live (on-line) monitoring of a biogas plant to be beneficial, the sensor response time must be improved, which is presented as an essential parameter that needs to be well adjusted. This can be achieved by investigating a combination of both the sensor setup and data analysis method that can be automated as much as possible to reach a robust, stable, and linear sensor. Therefore, by exploiting the achieved results presented in this investigation through selecting suitable excitation wavelengths, the light source can be replaced, for instance, by (LEDs) light-emitting diodes. By combing multiple LEDs with different wavelengths, a price-efficient sensor can be obtained especially in industrial applications. This sensor improvement will allow biogas production, even on a small scale, to reduce the operational cost. Moreover, our self-programming software for data analysis has been optimized to be compatible with the sensor instruments.

4. Conclusions

Gasification processes and the usage of biomass gases as a source of renewable energy are an important technology especially at the present time to produce biofuels in addition to electricity and heat generation. The production of unwanted Tar is one of the problems concurrent with biomass gasification, where it causes many obstacles in the production of energy and fuel. The produced gas must be evaluated and its suitability must be ensured, before being used in many applications. 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 analyzing results. This offers not only the quantification but also the qualification of Tar compounds in gas-phase with only optical involvement in the measured gas producer. 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 on-line monitoring of gasifier tars. The achieved results show a high compatibility to other measurement techniques [7,10,17], but in our work, the combination of LIF technique and EEM analysis method has been developed by newly constructed design as robust instrumentation.

Experimentally, the approach of fluorescence spectroscopy of aromatics is followed in the hot processed gas. Modeled gases are four known PAH compounds resultant in the gasification process. Large polycyclic aromatics having three or more rings can be excited stronger than compounds with fewer rings. By determining the position of the fingerprint in the EEM of a mixture of PAHs, the corresponding compound can be identified as well as the concentrations. Where the analyzed EEMs present as reference providing fast feedback for efficient biomass. The integration into process control or regulation of the target sought and neural data analysis are expected in the near future.

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