International Journal of Design & Nature and Ecodynamics
Vol. 17, No. 6, December, 2022, pp. 973-978
Journal homepage: http://iieta.org/journals/ijdne

Spectroscopic Measurement of High Argon Jet Plasma Flow Rate for Methane Hydrate Decomposition

Ismail Rahim[1], Novriany Amaliyah[2*], Mohammad Ahsan S. Mandra[1], Shinfuku Nomura[3]

[1] Automotive Technology Vocational Education Department, Universitas Negeri Makassar, Makassar 90224, Indonesia
[2] Mechanical Engineering Department, Hasanuddin University, Bontomarannu, Gowa 92171, Indonesia
[3] Graduate School of Science and Engineering, Ehime University, Matsuyama 7908577, Japan

Corresponding Author Email: novriany@unhas.ac.id

https://doi.org/10.18280/ijdne.170620

Received: 24 June 2022
Accepted: 10 October 2022

Keywords:
plasma, excitation temperature, spectrum emission, Boltzmann's plot, methane hydrate, argon jet

ABSTRACT

Methane hydrate is believed to contain a massive amount of potentially extractable hydrogen gas due to methane as the main component. A high-frequency argon jet plasma method has been proposed for decomposing hydrogen content. The excitation temperature of plasma can be directly observed from atomic emission lines. This information is more efficient to characterize the plasma behavior to optimize the decomposition process. In this study, the plasma excitation temperature was determined using spectroscopy and Boltzmann's plot with a higher argon gas flow rate. An argon gas flow rate varied from 300, 400, 500, 1000, 1500, 2000, 2500, and 3000 mL/min. It flows inside a hollow tube in the counter electrode. A 27.12MHz high-frequency power source of plasma was applied to produce jet plasma at atmospheric pressure. The excitation temperature was observed in the range of 4310K to 5133K. The highest excitation temperature of 5133K was obtained at an argon gas flow rate of 500 mL/min.

1. INTRODUCTION

During recent years, there has been an increasing interest in plasma technology on account of the adaptability of its application in nanoparticle production [1-3], surface and coating modification [4-6], sterilization [7], fuel gas and hydrogen production [8-11] to name a few. A higher production rate, more straightforward reaction mechanism, and high reactivity that enhance the chemical reaction rate are some of the advantages of using plasma technology. Plasma can generate under atmospheric pressure and higher pressure. There is an increasing concern about the advancement of plasma-generating technologies under atmospheric pressure [4, 12-15].

Plasma jet technology is one of thermal plasma processing with high speed and high heat capacity. In this method, plasma was penetrated and propagated inside small holes and flexible dielectric tubes. Research on plasma jet application has been carried out in many applications. Deposition of diamond-like carbon (DLC) layer as a hydrophobic film on cotton textile has been reported using atmospheric argon plasma jet [16]. Cold argon plasma jet at atmospheric pressure was applied for the inactivation of microorganisms [17]. The argon plasma jet was also introduced as an effective apparatus and a favorite for research in plasma medicine science [18, 19]. Production of high-purity carbon nanotubes by methane decomposition is conducted using an arc-jet plasma of high temperature [20]. An investigation of the argon gas flow rate effect in methane decomposition using catalytic pulsed plasma reported that the highest methane conversion and hydrogen production occurs at an argon flow rate of 70 mL/min [21].

Methane hydrate is a massive reserve in the world as a hydrogen energy resource. It originates on the ocean floor under strict environments of pressure and temperature. A considerable number of works of literature have been published on the decomposition of methane hydrate. Fluidized bed application in the thermal decomposition of methane can provide up to 40% of hydrogen. The effect of catalyst, temperature, and residence time was investigated. The result shows that black pearl 2000 was the best catalyst, the optimum operating temperature was 920-940°C, and increasing residence time by 90% will increase hydrogen concentration [22]. Hydrogen and carbon dioxide could be reformed in an endothermic process by sequestering carbon dioxide. The objective of this simulation plan is to produce hydrogen without the release of CO_2 into the atmosphere [23].

The In-liquid plasma method is simultaneously developed in the hydrogen production from methane hydrate. Our previous work confirmed that microwave and high-frequency irradiation plasma decomposition can produce hydrogen with a purity of 42 to 63% [18]. However, the high-pressure condition was hard to achieve using this apparatus. When applying argon jet plasma, a higher pressure up to 2.0MPa, which Argon as the carrier gas under a flow rate of 200mL/min, resulted in less hydrogen production efficiency [24].

Likewise, some parameters in plasma processing such as ionization, dissociation, and excitation are essential to understand related to plasma science, and optical emission spectroscopy is one of the techniques to determine those parameters. The excitation temperature is describing the plasma discharge and characterizes a population of excited atomic levels [25]. The free electron motion temperature is usually related to the electronic excitation temperature (Texc) of the bound electrons in an atom or molecule since the excitation processes that determine the distribution of excited states are mainly driven by free electrons [20]. Since electronic and thermal reactions become an important role in decomposition, the knowledge of the electron number density and the neutral gas temperature in the plasma is therefore essential for finding the chemical dynamics and optimization of gas decomposition [26].

Stark broadening is an excellent approach for electron measurement among various techniques owing to the independence from local thermal equilibrium (LTE), ingenious procedure, and the availability of suitable theoretical stark broadening line profiles for emission lines of hydrogen, helium, and argon [27].

Moreover, as an inert gas, Argon has an appropriate atomic mass amongst noble gases. It has been widely used for many applications due to this characteristic. A previous study reported the electron temperature and number density at constant input power and flow rate of 2.45GHz microwave argon plasma [26]. An excitation temperature at 7000K was determined at atmospheric pressure microwave argon plasma with a gas flow rate of 100 and 200mL/min [28, 29].

In this study, the experiment was performed by generating an argon jet plasma at a higher flow rate to determine the excitation temperature using spectrometry and Boltzmann's plot method. The observation of plasma behavior becomes essential to optimize the efficiency of hydrogen production from methane hydrate.

2. EXPERIMENTAL PROCEDURES

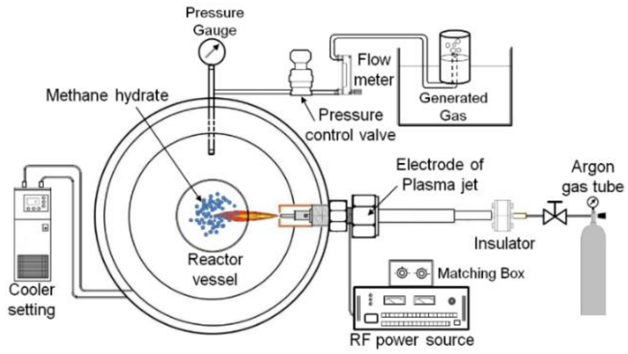

Figure 1. High-frequency argon jet plasma mechanism

The experimental procedures of the argon plasma jet is the same as in previous work [24], as shown in Figure 1. Plasma was generated to an electrode using a 27.12MHz high-frequency power source (T161-5766LQ, Thamway). An argon gas flow rates was varied from 300, 400, 500, 1000, 1500, 2000, 2500, and 3000mL/min. It discharged through a hollow tube made from stainless steel. The input power of plasma jet was set to 250W, and after its initiation, the pressure was adjusted to atmospheric pressure.

Figure 2 shows a multichannel spectrum analyzer (Hamamatsu Photonics-PMA 11 C7473-36). The input signal pulses and emission spectroscopy from the plasma irradiation was measured [30]. It is commonly used to digitize a large number of spectroscopic experiments, such as nuclear physics and including various types of spectroscopies.

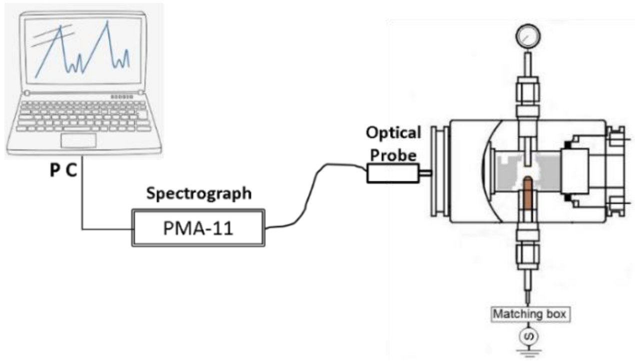

Figure 2. Multichannel spectral analyzer

3. RESULTS AND DISCUSSION

A Boltzmann diagram was set up from the net intensity of the argon I line. Such diagrams show the distribution of atoms at various energy levels as a function of energy and temperature. The equation of Boltzmann's plot is as follows:

$$ln\left(\frac{I_{ij}\,\boldsymbol{\lambda}_{ij}}{g_i\,\mathbf{A}_{ij}}\right)=\frac{\mathbf{E}_{ij}}{k.\mathbf{T}_{exc}}$$

where, E_i=upper-level energy (cm^{-1}); k=Boltzmann constant; g_i=statistical weight of the upper level; A_{ij}=transition probability (nm); I_{ij}=emission intensity of line; λ_{ij}=wavelength (nm).

These spectra lines are then used to estimate the excitation temperature. The list of selected argon lines with the configuration of the upper level is shown in Table 1.

Figure 3 shows observation of Argon I lines from argon plasma jet. It was found that the wavelength ranges from 706.7 to 922.4nm. A previous study confirmed when a high argon flow rate of 100 and 200L/min was applied using a microwave plasma source, the emission spectra at the range of 300 to 600nm were recorded [28]. Following the present results, the previous study has demonstrated a micro discharge of argon at various pressure. It was found that the emission intensity of Argon lines was from 400 to 820nm correlates with the 5p-4s and 4p-4s transition. This condition indicated a high electron temperature in the observed region [31].

Table 1. Spectral lines of argon I

No.	Substance	Wavelength	Configuration of upper level
1.	Argon I	706.7 nm	$3s^23p^4[^3P]5p \rightarrow 3s^23p^4[^3P]5d$
2.	Argon I	738.4 nm	$3s^23p^5[^2P°_{3/2}]4s \rightarrow 3s^23p^5[^2P°_{1/2}]4p$
3.	Argon I	763.5 nm	$3s^23p^5[^2P°_{3/2}]4s \rightarrow 3s^23p^5[^2P°_{3/2}]4p$
4.	Argon I	801.5 nm	$3s^23p^5[^2P°_{3/2}]4s \rightarrow 3s^23p^5[^2P°_{3/2}]4p$
5.	Argon I	811.5 nm	$3s^23p^5[^2P°_{3/2}]4s \rightarrow 3s^23p^5[^2P°_{3/2}]4p$
6.	Argon I	842.5 nm	$3s^23p^5[^2P°_{3/2}]4s \rightarrow 3s^23p^5[^2P°_{3/2}]4p$
7.	Argon I	852.1 nm	$3s^23p^5[^2P°_{1/2}]4s \rightarrow 3s^23p^5[^2P°_{1/2}]4p$
8.	Argon I	912.3 nm	$3s^23p^5[^2P°_{3/2}]4s \rightarrow 3s^23p^5[^2P°_{3/2}]4p$
9.	Argon I	922.4 nm	$3s^23p^5(^2P°_{1/2})4s \rightarrow 3s^23p^5(^2P°_{3/2})4p$

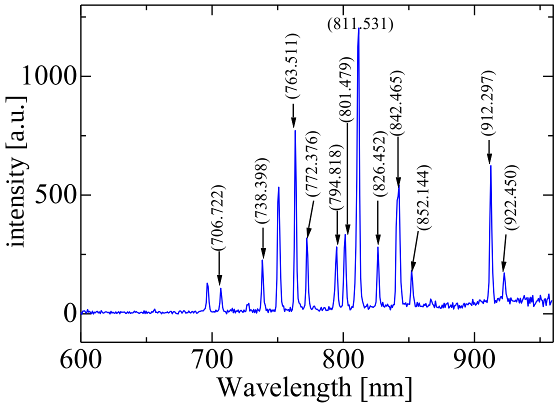

Figure 3. The emission line spectrum of Argon I from argon plasma jet under atmospheric pressure

Furthermore, excitation temperature is one of the plasma parameters describing an inhabitant of excited atomic levels. It may be more efficient to identify plasmas at both low- and high-pressure plasmas. Emission of atomic beam can be recognized by its transition both in low and high energy. High-frequency plasma discharge consists of two mechanisms, which are the collision between electrons and atoms of the background gas and the voltage across the sheaths [32]. In high-frequency plasma, collisional excitation was assumed to be predominant [33].

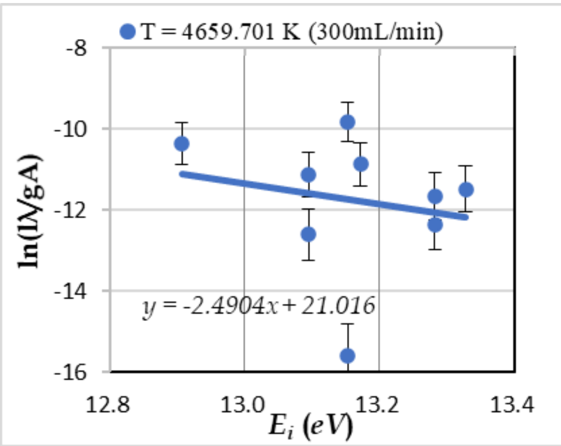

Figure 4. Excitation temperature at 300mL/min

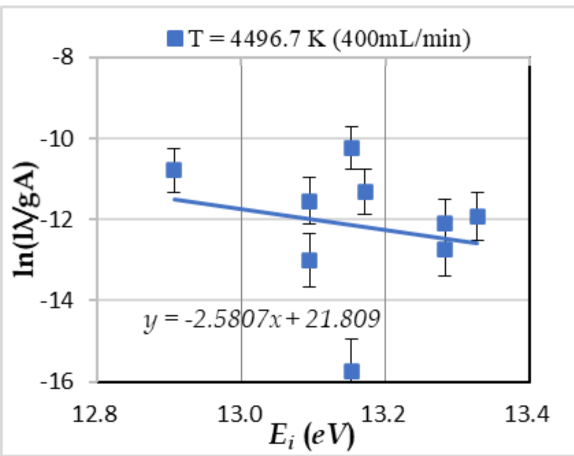

Figure 5. Excitation temperature at 400mL/min

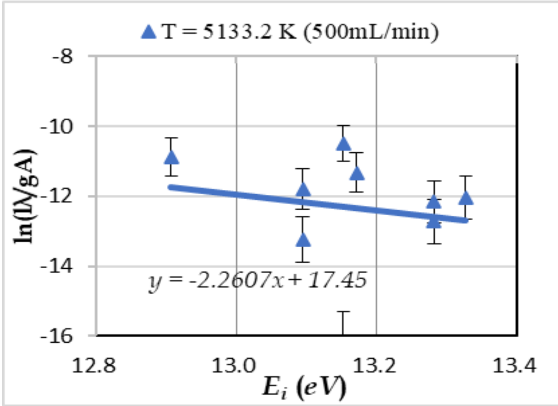

Figure 6. Excitation temperature at 500mL/min

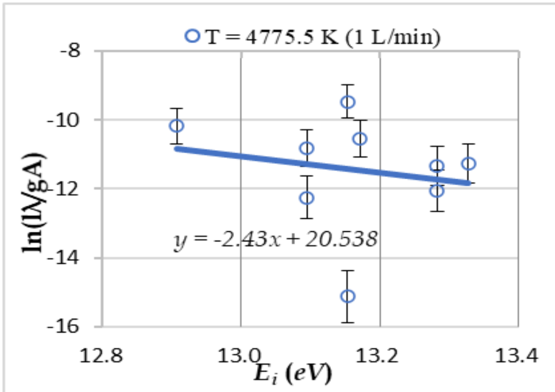

Figure 7. Excitation temperature at 1 L/min

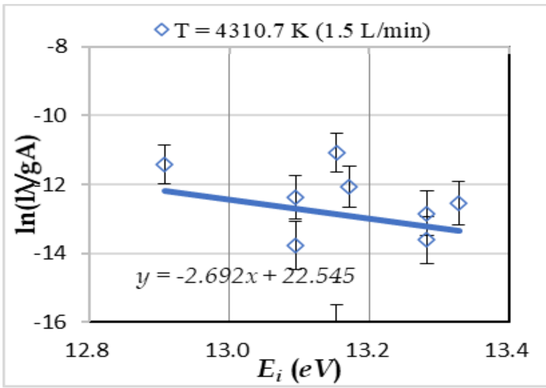

Figure 8. Excitation temperature at 1.5 L/min

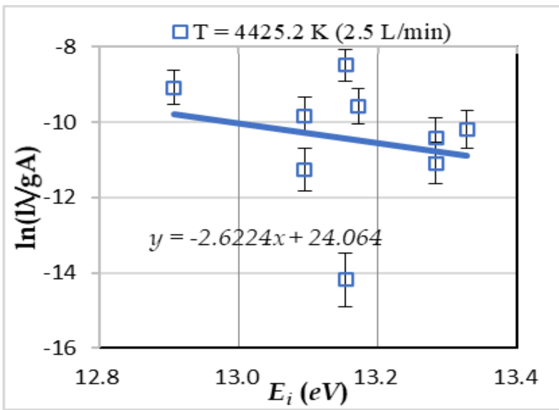

Figure 9. Excitation temperature at 2.5 L/min

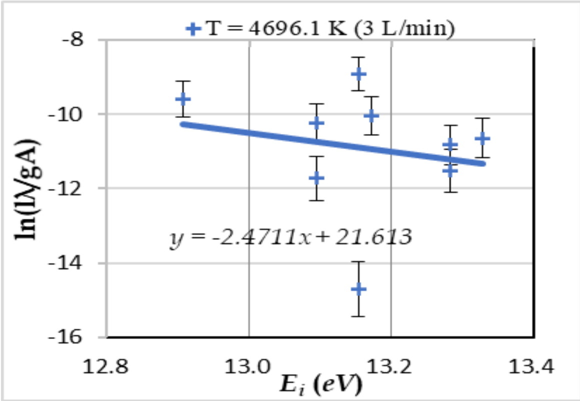

Figure 10. Excitation temperature at 3 L/min

As well, it is necessary to measure an excitation temperature to clarify the quality of the generated plasma. The spectroscopic properties were referred to the database from the National Institute Standards and Technology (NIST) [34]. Since the collisional excitation coefficient (Cij) is higher than the transition probability (Aj), Boltzmann's plot method for temperature measurement is applicable. Figure 4 to Figure 10 displays the excitation temperature determines by Boltzmann's plot from the net intensity of Argon I lines at various argon gas flow rates.

High-frequency plasma irradiation was performed under atmospheric pressure with an argon flow rate of 300-3000ml/min, and the excitation temperature was in the range of 4310K-5133K. The highest excitation temperature was obtained at the argon flow rate of 500mL/min. In comparison, at atmospheric pressure, the excitation temperature when using argon jet plasma was approximately 15% higher, and plasma irradiation was more stable than in the previous study when using high-frequency in-liquid plasma [15]. In the last study, an increase in excitation temperature was obtained when gas pressure was a rise in consequence of a higher frequency of electron collision. At high pressure with 2082K to 3960K of excitation temperature, hydrogen decomposition from methane hydrate was found to be relatively low than when methane hydrate was decomposed at atmospheric pressure with excitation temperature around 3500K [24]. Another study reported that excitation temperature measurement using 1.33g/s of the flow rate of argon jet plasma tended to rise higher than 6000K around the central position of the jet when a strong magnetic field was applied. However, toward the outer side of the jet, the considerable temperature declined [35].

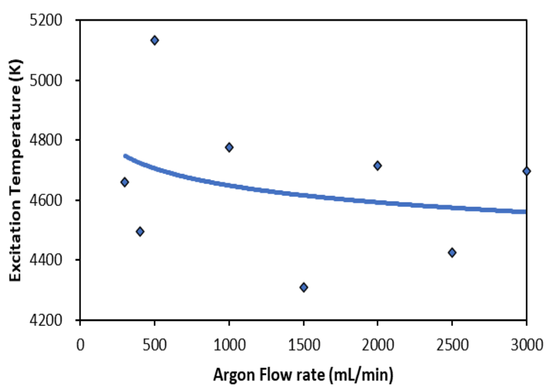

Figure 11. Optical emission intensity of Argon I line with various argon flow rate

Table 2 and Figure 11 show the disparity in emission intensities of several Argon I line as a function of argon gas flow rate. The reduction in excitation temperature with increasing pressure has been reported elsewhere [36]. The trend of the excitation temperature also decreases as the increase of argon gas flow rate. However, the plasma irradiation is more stable observed by the naked eye. When increasing the pressure, the stability of plasma irradiation is relatively difficult to obtain [8]. Since methane hydrate is stable under high pressure, an appropriate plasma behaviour, in this case, the excitation temperature, must confirm this condition.

Table 2. Measured excitation temperature at various argon flow rate

Argon Flow rate [mL/min]	T_{exc} [K]	T_{exc} [°C]
300	4660	4387
400	4497	4224
500	5133	4860
1000	4776	4502
1500	4311	4038
2000	4715	4442
2500	4425	4152
3000	4696	4423

4. CONCLUSIONS

The excitation temperature of the plasma is one of the essential parameters to clarify the quality of plasma. To optimize the hydrogen decomposition from methane hydrate, an appropriate excitation temperature should be achieved. In this research, an argon jet plasma was generated at a higher argon flow rate to determine the excitation temperature. In the range of 4310K to 5133K, excitation temperature was measured using Boltzmann's plot at an argon flow rate ranging from 300 to 3000mL/min. The highest excitation temperature was observed at 5133.2K with an argon gas flow rate of 500mL/min. The present result enlightens the excitation temperature fluctuation at a higher flow rate of argon jet plasma which can be valuable information to maximize the decomposition process.

ACKNOWLEDGMENT

This work is supported by the Indonesian Ministry of Research and Technology (Grant numbers: 81/UN.36.9/PL/2019).

REFERENCES

[1] Amaliyah, N., Mukasa, S., Nomura, S., Toyota, H., Kitamae, T. (2015). Plasma in-liquid method for reduction of zinc oxide in zinc nanoparticle synthesis. Materials Research Express, 2(2): 025004. https://doi.org/10.1088/2053-1591/2/2/025004

[2] Hattori, Y., Nomura, S., Mukasa, S., Toyota, H., Inoue, T., Usui, T. (2013). Synthesis of tungsten oxide, silver, and gold nanoparticles by radio frequency plasma in water. Journal of Alloys and Compounds, 578: 148-152. https://doi.org/10.1016/j.jallcom.2013.05.032

[3] Purohit, V.S., Dey, S., Bhattacharya, S.K., Kshirsagar, A., Dharmadhikari, C.V., Bhoraskar, S.V. (2008). ECR plasma assisted deposition of zinc nanowires. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 266(23): 4980-4986. https://doi.org/10.1016/j.nimb.2008.08.016
[4] Nagasawa, H., Xu, J., Kanezashi, M., Tsuru, T. (2018). Atmospheric-pressure plasma-enhanced chemical vapor deposition of UV-shielding TiO_2 coatings on transparent plastics. Materials Letters, 228: 479-481. https://doi.org/10.1016/j.matlet.2018.06.053
[5] Yu, H.C., Suo, X.K., Gong, Y.F., Zhu, Y.J., Zhou, J., Li, H., Eklund, P., Huang, Q. (2016). Ti_3AlC_2 coatings deposited by liquid plasma spraying. Surface and Coatings Technology, 299: 123-128. https://doi.org/10.1016/j.surfcoat.2016.04.076
[6] Eslamian, M. (2014). Spray-on thin film PV solar cells: Advances, potentials, and challenges. Coatings, 4(1): 60-84. https://doi.org/10.3390/coatings4010060
[7] Decina, A., D'Orazio, A., Barni, R., Polissi, A., Riccardi, C. (2021). A plasma reactor for experimental investigation of sterilization processes: Preliminary results on Escherichia coli. International Journal of Design & Nature and Ecodynamics, 16(3): 275-284. https://doi.org/10.18280/ijdne.160305
[8] Rahim, I., Nomura, S., Mukasa, S., Toyota, H. (2014). A comparison of methane hydrate decomposition using radio frequency plasma and microwave plasma methods. The 15th International Heat Transfer Conference, pp. 1-10. http://dx.doi.org/10.1615/IHTC15.pls.009897
[9] Ismail, R., Shinfuku, N., Shinobu, M., Hiromichi, T. (2015). Fuel gas production from biomass sources by radio frequency in-liquid plasma method. Journal of Power and Energy Engineering, 3(8): 28-35. https://doi.org/10.4236/jpee.2015.38004
[10] Erwin Eka Putra, A., Nomura, S., Mukasa, S., Toyota, H. (2014). Hydrogen production by reforming clathrate hydrates using the in-liquid plasma method. In Progress in sustainable energy technologies: Generating Renewable Energy, pp. 499-507. https://doi.org/10.1007/978-3-319-07896-0_30
[11] Syahrial, F., Mukasa, S., Toyota, H., Okamoto, K., Nomura, S. (2014). Hydrogen production from glucose and cellulose using radio frequency in-liquid plasma and ultrasonic irradiation. Journal of the Japan Institute of Energy, 93(11): 1207-1212. https://doi.org/10.3775/jie.93.1207
[12] Chiang, T., Richmonds, C., Sankaran, R.M. (2010). Microplasmas: A versatile source for metal nanoparticle synthesis in the gas or liquid. Plasma Sources Science and Technology, Article ID: 034011. https://doi.org/10.1088/0963-0252/19/3/034011
[13] Shirai, N., Uchida, S., Tochikubo, F. (2014). Synthesis of metal nanoparticles by dual plasma electrolysis using atmospheric dc glow discharge in contact with liquid. Japanese Journal of Applied Physics, 53(4): 046202. https://doi.org/10.7567/JJAP.53.046202
[14] Kim, J., Katsurai, M., Kim, D., Ohsaki, H. (2008). Microwave-excited atmospheric-pressure plasma jets using a microstrip line. Applied Physics Letters, 93(19): 191505. https://doi.org/10.1063/1.3025841
[15] Nomura, S., Mukasa, S., Toyota, H., Miyake, H., Yamashita, H., Maehara, T., Kawashima, A., Abe, F. (2011). Characteristics of in-liquid plasma in water under higher pressure than atmospheric pressure. Plasma Sources Science and Technology, 20(3): 034012. https://doi.org/10.1088/0963-0252/20/3/034012
[16] Sohbatzadeh, F., Shakerinasab, E., Eshghabadi, M., Ghasemi, M. (2019). Characterization and performance of coupled atmospheric pressure argon plasma jet with n-hexane electrospray for hydrophobic layer coatings on cotton textile. Diamond and Related Materials, 91: 34-45. https://doi.org/10.1016/j.diamond.2018.10.023
[17] Baldanov, B.B., Ranzhurov, T.V., Semenov, A.P., Gomboeva, S.V. (2019). Cold atmospheric argon plasma jet source and its application for bacterial inactivation. Journal of Theoretical and Applied Physics, 13(2): 95-99. https://doi.org/10.1007/s40094-019-0326-3
[18] Rafiei, A., Sohbatzadeh, F., Hadavi, S., Bekeschus, S., Alimohammadi, M., Valadan, R. (2020). Inhibition of murine melanoma tumor growth in vitro and in vivo using an argon-based plasma jet. Clinical Plasma Medicine, 19: 100102. https://doi.org/10.1016/j.cpme.2020.100102
[19] Miebach, L., Freund, E., Clemen, R., Weltmann, K.D., Metelmann, H.R., von Woedtke, T., Gerling, T., Wende, K., Bekeschus, S. (2022). Conductivity augments ROS and RNS delivery and tumor toxicity of an argon plasma jet. Free Radical Biology and Medicine, 180: 210-219. https://doi.org/10.1016/j.freeradbiomed.2022.01.014
[20] Choi, S.I., Nam, J.S., Lee, C.M., Choi, S.S., Kim, J.I., Park, J.M., Hong, S.H. (2006). High purity synthesis of carbon nanotubes by methane decomposition using an arc-jet plasma. Current Applied Physics, 6(2): 224-229. https://doi.org/10.1016/j.cap.2005.07.045
[21] Ghanbari, M., Binazadeh, M., Zafarnak, S., Taghvaei, H., Rahimpour, M.R. (2020). Hydrogen production via catalytic pulsed plasma conversion of methane: Effect of $Ni–K_2O/Al_2O_3$ loading, applied voltage, and argon flow rate. International Journal of Hydrogen Energy, 45(27): 13899-13910. https://doi.org/10.1016/j.ijhydene.2020.03.099
[22] Dunker, A.M., Kumar, S., Mulawa, P.A. (2006). Production of hydrogen by thermal decomposition of methane in a fluidized-bed reactor—Effects of catalyst, temperature, and residence time. International Journal of Hydrogen Energy, 31(4): 473-484. https://doi.org/10.1016/j.ijhydene.2005.04.023
[23] Rice, W. (2006). Hydrogen production from methane hydrate with sequestering of carbon dioxide. International Journal of Hydrogen Energy, 31(14): 1955-1963. https://doi.org/10.1016/j.ijhydene.2006.01.017
[24] Rahim, I., Nomura, S., Mukasa, S., Toyota, H. (2015). Decomposition of methane hydrate for hydrogen production using microwave and radio frequency in-liquid plasma methods. Applied Thermal Engineering, 90: 120-126. https://doi.org/10.1016/j.applthermaleng.06.074
[25] Ismail, R., Shinfuku, N., Shinobu, M., Hiromichi, T., Muhammad, A., Novriany, A. (2017). Application of argon plasma jet for methane hydrate decomposition by radio frequency irradiation. International Journal on Advanced Science Engineering Information Technology, 7(6): 2092-2099. http://eprints.unm.ac.id/id/eprint/21547.
[26] Deeba, F., Qayyum, A., Mahmood, N. (2015). Optical emission spectroscopy of 2. 45 GHz microwave induced plasma. Journal of Research in Spectroscopy, 2015:

172302. https://doi.org/10.5171/2015.172302
[27] Imran, M., Rehman, N.U., Zaka-ul-Islam, M., Shafiq, M., Zakaullah, M. (2016). Correlation between excitation and electron temperature in 50 Hz pulsed ArO_2 mixture plasma. Optik, 127(6): 3312-3315. https://doi.org/10.1016/j.ijleo.2015.12.068
[28] Miotk, R., Hrycak, B., Jasinski, M., Mizeraczyk, J. (2012). Spectroscopic study of atmospheric pressure 915 MHz microwave plasma at high argon flow rate. In Journal of Physics: Conference Series, 406(1): 012033. https://doi.org/10.1088/1742-6596/406/1/012033
[29] Yugeswaran, S., Selvarajan, V. (2006). Electron number density measurement on a DC argon plasma jet by stark broadening of Ar I spectral line. Vacuum, 81(3): 347-352. https://doi.org/10.1016/j.vacuum.2006.06.001
[30] Adrian, J.N., Melissinos, Mca, T. (2003). Experiments in Modern Physics, 2nd ed. Academic Press.
[31] Sismanoglu, B.N., Cunha, C.L.A., Gomes, M.P., Caetano, R., Grigorov, K.G. (2010). Optical and electrical diagnostics of microdischarges at moderate to high pressure in argon. Brazilian Journal of Physics, 40: 459-463. https://doi.org/10.1590/S0103-97332010000400018
[32] Lister, G.G., Li, Y.M., Godyak, V.A. (1996). Electrical conductivity in high-frequency plasmas. Journal of Applied Physics, 79(12): 8993-8997. https://doi.org/10.1063/1.362631
[33] Ohno, N., Razzak, M.A., Ukai, H. (2006). Validity of electron temperature measurement by using boltzmann plot method in radio frequency inductive discharge in the atmospheric pressure range. Plasma and Fusion Research, 1: 1-9.
[34] Physical Measurement Laboratory. (2010). NIST: Atomic Spectra Database Lines Form.
[35] Koike, K., Ono, N., Watanabe, Y., Musha, K. (2004). Measurement on the excitation temperature of argon plasma jet under strong magnetic field. Vacuum, 73(3-4): 353-358. https://doi.org/10.1016/j.vacuum.2003.12.055
[36] Park, H., Choe, W. (2010). Parametric study on excitation temperature and electron temperature in low pressure plasmas. Current Applied Physics, 10(6): 1456-1460. https://doi.org/10.1016/j.cap.2010.05.013