

THE APPLICATION OF LASER IN THERMAL TREATMENT OF SOLID PARTICLES AND GAS-PHASE OF BIOMASS PROCESSING-A REVIEW

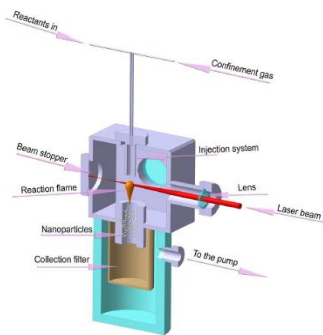
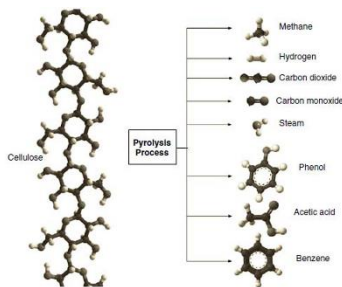
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Graphical abstract



Abstract

Application of laser in heating technique of both organic gas-phase and solid particles for thermochemical decomposition at elevated temperatures in the absence of oxygen is presently a challenging area. Laser pyrolysis is a powerful and a versatile tool for the gas-phase synthesis of nanoparticles. Generally, the purpose of pyrolysis is not only for energy production but also for the production of chemical feedstocks. This paper reviews on the pyrolysis activities, generally in Malaysia and the utilization of laser in pyrolysis for renewable energy and materials application. Malaysia is a well-known for palm oil producer country in the world, generating significant wastes yearly from oil palm mills such as empty fruit bunch (EFB), shell, fiber and palm oil mill effluent (POME) has put the government to solve these wastes problem by doing research on the development of renewable energy and materials. This reviews concluded that there are new area of research for the utilization of waste material by using laser technique.

Keywords: Laser pyrolysis, pyrolysis, renewable energy, waste material

Abstrak

Penggunaan laser dalam teknik pemanasan untuk bahan organik fasa gas dan zarah pepejal untuk penguaraan termokimia pada suhu tinggi dalam keadaan tiada oksigen pada masa kini adalah bidang yang mencabar. Pirolisis laser adalah alat yang berkuasa dan serba boleh bagi sintesis bahan nanopartikel dalam fasa gas. Secara amnya, tujuan pirolisis bukan sahaja untuk penghasilan tenaga, tetapi juga untuk penghasilan bahan mentah kimia. Kertas kerja ini mengulas tentang aktiviti-aktiviti pirolisis secara amnya di Malaysia dan penggunaan laser dalam pirolisis untuk tenaga yang boleh diperbaharui dan aplikasi bahan. Malaysia terkenal sebagai pengeluar minyak sawit utama dunia yang menghasilkan banyak bahan buangan tahunan daripada kilang kelapa sawit seperti tandan kosong kelapa sawit (EFB), tempurung kelapa sawit, serat, dan efluen kilang kelapa sawit(POME) telah meletakkan kerajaan ke arah menyelesaikan masalah sisa buangan ini dengan melakukan kajian terhadap pembangunan tenaga dan bahan yang boleh diperbaharui di Malaysia. Ulasan kajian ini telah menyimpulkan bahawa terdapat satu bidang kajian yang baharu untuk pengitaran semula bahan buangan dengan menggunakan teknik laser.

Kata kunci: Pirolisis laser, pirolisis, tenaga yang boleh diperbaharui, bahan buangan

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1.0 INTRODUCTION

Nowadays, laser has been widely used since it was introduced in 1958. Starting from the year many scientific, military, medical and commercial laser applications have been developed.

In science, laser are used in many ways such as in spectroscopy [1-5], microscopy [6-9], photochemistry [10-12], barcode scanner, heat treatment [13-15] and extra. Laser can be a good energy weapon for the military and basically laser used to be a pointer guide for targeting. It is not impossible in the future, laser can produced such energy bullet to shoot airplane in the sky. In terms of medical application, laser was used for surgery [16-17], removing scars [18-20], stretch mark, wrinkles and extra.

Industrial laser applications can be divided into two categories depending on the power of the laser, material processing and micro-material processing. In material processing, lasers with average optical power above 1 kilowatt are used mainly for industrial materials processing applications. Laser systems in the 50-300W range are used primarily for pumping, plastic welding and soldering applications. Lasers above 300W are used in brazing, thin metal welding, and sheet metal cutting applications [21]. Micro material processing is a category that includes all laser material processing applications under 1 kilowatt [22]. The use of lasers in Micro Materials Processing has found broad application in the development and manufacturing of screens for smartphones, tablet computers, and LED TVs [23].

Presently, there are many new researches ongoing utilizing laser as a tool for the new applications. Thermal treatment using laser is a new key area where heat produce in a random motion of matter particles (atomic or molecular particles) and the laser beam itself is not made of matter but of 'photons' [24], the so called 'light particles' which have no mass and the laser beam can have no temperature. The unique of laser thermal treatment characteristics derived to the implementation of laser pyrolysis. Pyrolysis is a well-known technology and its conversion of solid waste to renewable energy and materials have been done using microwave technique (MW) [25-32], plasma [33-35] and laser [36-46], [80-82].

2.0 RENEWABLE ENERGY SOURCES

Studies on biomass waste from oil palm shell, coconut shell, rubber tree and others can be found in most of journals publication. Oil palm shell producing only 10% of palm oil and the rest is biomass therefore, oil palm industries produce more residues compare to other industries. Converting biomass to electricity or steam is among the famous research area that have been done and discussed over the world.

Nowadays, biomass is considered as one of the main sources of energy for both developed and developing countries. Malaysia with a large amount of biomass residues as a source of electricity generation

is considered as one of the potential countries in this field. This will contribute substantially to harness a sustainable resource management system in Malaysia to reduce the major disposal problem of biomass residue. The effective use of the waste can supply the required fuel for future electricity generation [47].

The demand of electricity was increased in line with the world population and economic growth in developing countries [48]. Malaysia was also not spared from this situation and statistics from Figure 1 explains everything.

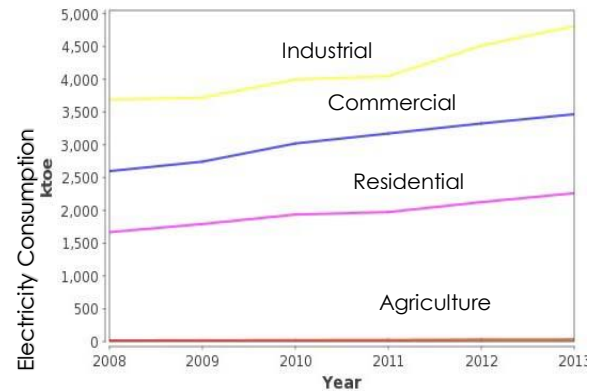


Figure 1 Final electricity consumption (ktoe) from 2008 to 2013 in Malaysia

The limitation of fossil fuel sources and the awareness of climate changes drive the government to shift the energy policy towards the other source of energy. Biomass residue is a promising fuel source for electricity generation that can reduce the CO₂ emission simultaneously [49]. Biomass energy is the most potential energy source in Malaysia to overcome the increasing energy needs while preserving the environment [50]. In spite of oil palm biomass and other solid wastes in Malaysia as renewable energy source, rubber and rice husk could be a potential source of alternative energy, fuel and chemical [51-55]. Currently, researcher is focusing towards the hydrogen production from biomass resources since it is expected to become a major source of energy.

In addition to power generation, biomass can be converted to bio-fuel such as bio-diesel, bio-ethanol and bio-methanol either in slow or fast pyrolysis techniques. For an example Ani *et al.* [56] had characterized bio-oils from oil palm biomass from different fast pyrolysis techniques. Motasemi and Ani [57] had reviewed papers regarding the microwave-assisted technique as an attempt to find a way to reduce the production cost and produce a higher quality biodiesel. They emphasis biodiesel is a potential substitute for diesel engines and the adoption of this fuel has some primary advantages such as the environmental benefits of reducing emissions and amelioration of national energy security through a reduction in the fossil fuel consumption. Malaysia and

Indonesia lead to be the country that utilize biomass from oil palm shell for biodiesel significantly [58]. A comprehensive review on biodiesel as an alternative energy resource and its characteristics was done by Atabani *et al.* [59]. In their review they have elaborated the need of alternative diesel to be replaced by biodiesel from various agriculture waste. Bio-ethanol was made from sago pith waste (SPW) sago 'hampas' is a fibrous starchy lignocellulosic by product generated from pith of Metroxylon sago (sago palm) by Saravana *et al.* [60]. They have used microwave hydrothermal hydrolysis technique with CO_2 , as a result maximum of 43.8% glucose and 15.6 g ethanol per 100 g SPW was obtained. Bio-ethanol from agro-residues could be a promising technology that involves four processes of pre-treatment, enzymatic hydrolysis, fermentation and distillation [61]. The worldwide bio-ethanol production is increasing constantly because of the increasing demand. Traditionally sugarcane and sugar beets are major traditional agricultural crops used as bio-ethanol production but unable to meet the demand. Therefore the utilization of agro-residues as bioethanol is the right choice. Converting agriculture waste to bio-methanol which can be used to generate electricity and power for portable applications was discussed in terms of different processes that have been developed for the production of bio-methanol [62].

Activated carbon is one of the application derived from the utilization of biomass but other material such as coal could be also change to activated carbon [63]. A lot of researchers, doing an intensive research in this area. Activated carbon is a porous material produced from various carbonaceous materials. Two process has to be implemented which are carbonization and activation process before activated carbon was produced. Carbonization is a process by which solid residues with increasing content of the element carbon are formed from organic material usually by pyrolysis in an inert atmosphere whereas, activation is a process of water removal, conversion of the organic matter to element, driving off the nanocarbon portion and burning tars and pore enlargement. Carbonization itself can produced carbon molecular sieved (CMS) that usually used in gas separation [64]. Activated carbon has a wide range of application such as for medical use, analytical chemistry applications, environmental applications, agriculture use, fuel storage, gas purification, chemical purification, sound absorption and the latest is to produce green supercapacitor [65-66]. Basically, activation process can be divided into two types 1) Physical activation; 2) Chemical activation. Physical activation and chemical activation was done separately but sometimes in some cases both of the processes was done together in order to get more porosity.

Recently more researcher switch into a new method of activated carbon production. Instead of using conventional furnace they use microwave as the thermal source. A review has been done by Faisal *et al.* [32] to study on microwave assisted pyrolysis of coal

and biomass for fuel production. They concluded that microwave heating of coal or biomass particles with microwave absorber shows efficient heating and sufficient contact of volatile or gas phase species with specific microwave absorber can improve fuel quality. An experiment was done by Salema and Ani [29] to prove microwave assisted pyrolysis with microwave absorber is the best way of pyrolysis technique. Overall result show the low temperature microwave pyrolysis of oil palm shell (OPS) gave significant contribution in energy efficient route to bio-oil production. Moreover, use of eco-friendly microwave absorber can assist the microwave to operate at low power input, thus reducing the need for high power microwave pyrolysis.

Biomass gasification process is one of the significant area on the utilization of biomass. In the process, carbon monoxide (CO), Hydrogen (H_2) and traces of Methane (CH_4) are produced. The hydrocarbon gas not only can be converted into energy but also can be used as a source to produce carbon nanoparticles.

3.0 PYROLYSIS TECHNOLOGY

Prabir [67] defined that pyrolysis is a thermochemical decomposition of biomass into a range of useful products, either in the total absence of oxidizing agents or with a limited supply that does not permit gasification to an appreciable extent. It is one of several reaction steps or zones observed in a gasifier. During pyrolysis, large complex hydrocarbon molecules of biomass break down into relatively smaller and simpler molecules of gas and liquid.

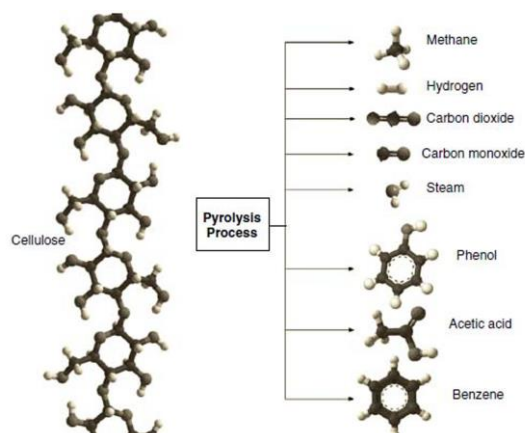


Figure 2 Process of decomposition of large hydrocarbon molecules into smaller one during pyrolysis

Pyrolysis has similarity to and some overlap with processes like cracking, devolatilization, carbonization, dry distillation, destructive distillation, and thermolysis. Normally, biomass pyrolysis is carried out in a relatively low temperature range of 300 to 650 °C compared to 800 to 1000 °C for gasification.

Based on heating rate, pyrolysis classified to two categories which are slow pyrolysis and fast pyrolysis.

Carbonization is a slow pyrolysis process, in which the production of charcoal or char is the primary goal whereas fast pyrolysis is to maximize the production of liquid or bio-oil as the primary goal.

3.1 Pyrolysis Researches

Slow pyrolysis process was done by Jun'ichi *et al.* [68] to prepare activated carbon from various nutshells. The impregnated nutshell (with K_2CO_3) was heated up to a carbonization temperature at a heating rate of 10 K/min and thereafter maintained for 60 min at that temperature under N_2 gas flow. The carbonization temperature of 773–1173 K were applied and they found that when prepared at 1073 K, the activated carbons from all the nutshells had the maximum specific surface areas. Meanwhile, agriculture waste from rice straw was investigated by Jinje *et al.* [69] in slow pyrolysis for temperatures of 300–700°C. The aim of their project is to characterize the yields and detailed composition of the biochar, bio-oil and non-condensable gases.

In terms of fast pyrolysis, Bridgwater [70] had reviewed a lot of publish journals on fast pyrolysis of biomass for production of a liquid usually referred to as bio-oil. He claimed that the accumulation of many liquid properties data, have caused increasingly extensive research to be undertaken to address properties that need modification and this area is reviewed in terms of physical, catalytic and chemical upgrading. Previously, Bridgwater *et al.* [71] were reviewed on the aspects of design of a fast pyrolysis system include feed drying; particle size; pre-treatment; reactor configuration; heat supply; heat transfer; heating rates; reaction temperature; vapour residence time; secondary cracking; char separation; ash separation; liquids collection.

Currently, microwave (MW) assisted pyrolysis was done by many researcher to study and investigated the role of microwave as a thermal source. Among of them are Salema and Ani [72-73], have done an experiment for oil palm shell biomass using an overhead stirrer. They concluded that MW pyrolysis with a stirrer successfully produced high-phenol bio-oil compared to other methods. Both of them also found that performance of stirred bed was better than fixed bed since the former showed complete pyrolysis within short time, which could be useful in saving time, energy and cost of the process [74]. Meanwhile Zubairu *et al.* [75] emphasis that the temperature profile, product yield and the properties of the products were found to depend on the stirrer speed and MW absorber percentage. Agricultural residues are abundant resources to produce renewable energy and valuable chemicals [76]. They have focused on the effects of lignocellulosic composition and microwave power level on the gaseous product of microwave pyrolysis of agricultural residues. Bio oil production by MW assisted pyrolysis also one of the famous product produced among the researcher Qinglong *et.al* [77]; Andrea *et al.* [78]; Faisal *et al.* [79]. All the research aim to support on the finding of

alternative fuel to overcome on the dependence to the fossil fuel.

Laser pyrolysis is one of another method could be the new invention on the study of biomass utilization. Since today, not so many researcher involved to promote the contribution of laser as a good thermal source especially for the pyrolysis application. Therefore more research should be done to study on the special characteristic for the application of laser pyrolysis.

4.0 LASER PYROLYSIS

There are a lot of research on laser pyrolysis presented in published journal which can be divided into several topics such as type of laser, implementation method and applications.

Laser is a device that generates an intense beam of coherent monochromatic light (or other electromagnetic radiation) by stimulated emission of photons from excited atoms or molecules. Lasers are used in drilling and cutting, alignment and guidance, and in surgery; the optical properties are exploited in holography, reading barcodes, and in recording and playing compact discs.

There are a lot of laser types such as gas lasers, chemical lasers, dye lasers, metal vapour lasers and extra. The carbon dioxide laser (CO_2 laser) was one of the earliest gas lasers to be developed (invented by Kumar Patel of Bell Labs in 1964), and is still one of the most useful. Carbon dioxide lasers are the highest-power continuous wave lasers that are currently available. They are also quite efficient: the ratio of output power to pump power can be as large as 20%. The CO_2 laser produces a beam of infrared light with the principal wavelength bands centering around 9.4 and 10.6 micrometers (as in Figure3).

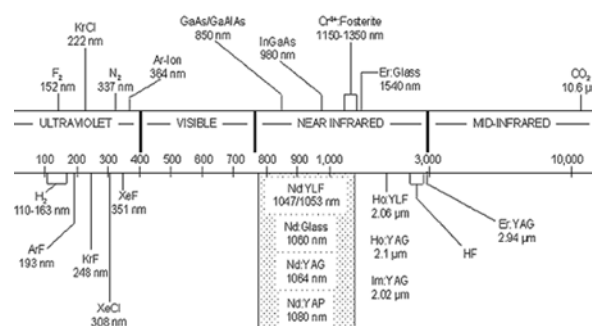


Figure 3 Laser wavelength chart

4.1 Researches and Patents

There are several journals and patents related to laser pyrolysis where most of the researchers uses CO_2 laser (either continues or pulse). Nanoparticle, carbon blacks and carbon nanotubes are the most popular subject in these research.

Carbon nanoparticles synthesised by laser pyrolysis of pure hydrocarbons in a flow reactor have been investigated as a function of laser power by Aymeric *et al.* [36]. They have been setup an experimental rig for this IRLP (Infrared Laser Pyrolysis. IRLP is a versatile method for the production of a wide range of nanopowders [37–39]. In their research, the main objective is to contribute to the understanding of carbons resulting from pyrolysis of organic precursors at moderate temperature ($<1400\text{ }^{\circ}\text{C}$). Several hydrocarbon (C_4H_6 (butadiene), C_2H_4 (ethylene) or C_3H_4 (propadiene)) with an absorption band near $10.6\text{ }\mu\text{m}$ have been tested as precursors. In order to evaluate the best candidate, the threshold for flame apparition was measured as a function of the reactant flow. C_4H_6 appears to be the best precursor because a reaction occurs even at very low laser power.

Another research on the production of carbon nanoparticles was done by Ja'nger *et al.* [40] as shown in Figure 4 for the pyrolysis setup.

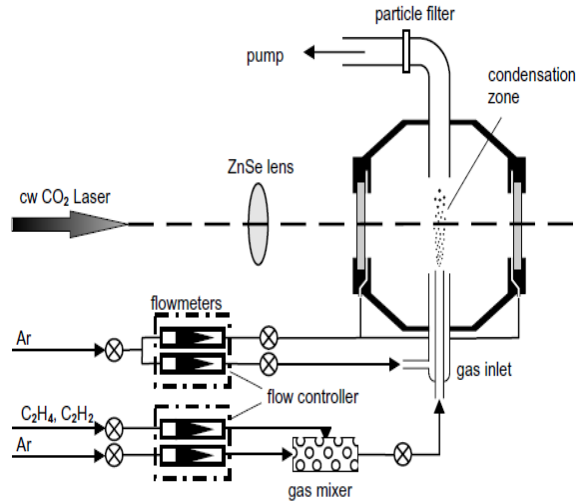


Figure 4 Schematic of the laser pyrolysis setup

CO_2 laser induced co-pyrolysis of toluene and iron pentacarbonyl in the presence of an ethylene sensitizer was used to produce iron-carbon nanostructures containing cementite Fe_3C as the major component. Due to the potential application in magnetic nanofluids, sensors, ceramic and catalysis sciences, iron-based nanoparticles system are being increasingly investigated. Ceramic nanoparticles was synthesized by CO_2 laser pyrolysis and the research has reported new results on the synthesis of SiC , TiO_2 and SiO_2 nanoparticles for energetic applications and cultural heritage preservation [41]. Schematic diagram for the experimental rig as shown in Figure 5.

Meanwhile, producing nanoscales carbon blacks by CO_2 laser pyrolysis have been done by Xiang *et al.* [42]. CO_2 laser pyrolysis has been used to synthesize carbon black (particle diameter $\sim 30\text{ nm}$) via a catalytically driven pyrolysis of benzene vapor. Furthermore, KOH treatment at $\sim 800^{\circ}\text{C}$ has been

employed to activate the particles. TEM images shows particles are nearly spherical, amorphous and slightly tendency to graphitize. Traditionally, carbon black has been used as a reinforcing agent in tires.

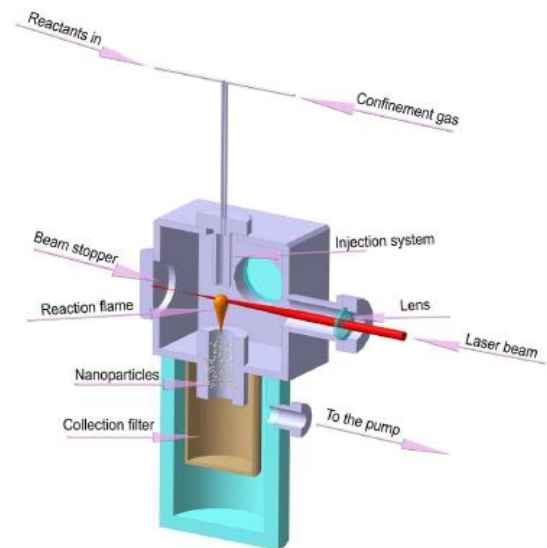


Figure 5 Schematic of the set-up for laser synthesis of nanoparticles from gas-phase reactants

Today, because of its unique properties, the uses of carbon black have expanded to include pigmentation, ultraviolet (UV) stabilization and conductive agents in a variety of everyday and specialty high performance products, including tires and industrial rubber products, plastics, electrostatic discharge (ESD) compounds, high performance coatings, toners for printing inks and extra. Research on carbon blacks expanding when Mordkovich *et al.* [43] do an observation of the nanostructure for multiwall fullerenes. Carbon blacks was produced from benzene with the assistance of an iron carbonyl catalyst. For others application laser pyrolysis can be used to produce chromium (III) oxide powders [44]. Schematic of the experimental rig shown as below.

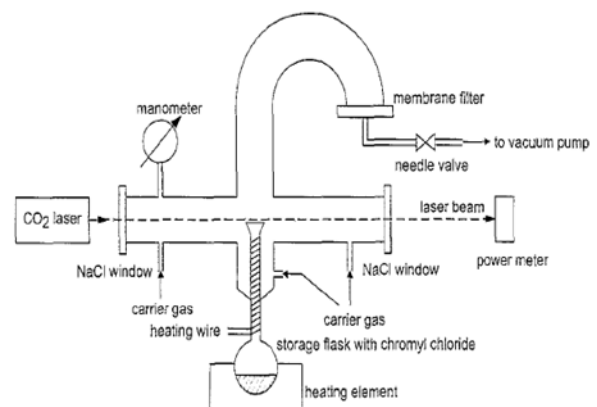


Figure 6 Schematic drawing of the flow reactor

The experiment shows that the pressure in the reaction chamber, focusing the laser beam or using different carrier gases has a significant influence on the mean particle size. Variation of the laser power and of the flow rate of the carrier gas does not influence the particle size. Coating removal of EN AW-5251 H34 aluminium magnesium alloy sheets [45] and removal of chlorinated rubber [46] another two example for laser pyrolysis application but in the experimental Nd:YAG laser and diode laser were used respectively.

Thomas, Andrew and Bryan invent on a novel method for the laser pyrolysis of relatively homogeneous samples of hollow carbon nanospheres and related intermediate products [80]. Due to their unique structural, mechanical and electronic properties and hence their potential for use in an important commercial applications have motivated them to fabricate the new carbon-based nanomaterials with highly curved graphitic structures.

Wang, Yang and Jing [81] present another invention relates to a carbon nanotube composite material and preparation method. They claimed that the carbon nanocomposite materials produced by them can be used to remove pollutants in wastewater and the removal efficiency was significantly higher than the existing nanomaterials.

High graphitization degree of preparation for carbon nanomaterials has been claimed by Jane *et al.* [82]. The invention methodology was described in the patent which included with type of gaseous, catalysts, chamber pressure and temperature.

5.0 CONCLUSIONS

Laser is a powerful tool and beneficial to human in various aspects of life and the latest research show that laser capable of producing carbon nanoparticles. Presently, the production of carbon nanoparticles is one of category in nanotechnology industry. It could be produced from solid particles or gas-phase of agricultural waste processing which could ensure the sustainability of the natural resources. Therefore, the use of laser in pyrolysis process is a relatively new method and a versatile thermal source which is easy to operate. In the future, laser technology is expected to contribute towards manufacturing science.

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