

**THE EFFECT COMBINATION OF ACID TREATMENTS
FOR SILICON CARBIDE (SiC) PRODUCTION FROM
RICE STRAW**

NORIDAYU BINTI ISMAIL

UNIVERSITI MALAYSIA PERLIS

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FOR SILICON CARBIDE (SiC) PRODUCTION FROM
RICE STRAW**

By

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LIST OF ABBREVIATIONS

NO

SiC	Silicon carbide
RS	Rice straw
SEM	Scanning electron microscopy
EFB	Empty fruit bunch
RH	Rice husk
SBRSA	Semi burned rice straw ash
CATS	Consecutive acid treated rice straw
RSM	Response surface methodology
FTIR	Fourier Transform Infrared
XRF	X-Ray florescent
XRD	X-Ray diffraction
UTRS	Untreated rice straw
CO	Carbon monoxide
kWh/kg	Unit for energy
W/cm-k	Unit for thermal conductivity
L/min	Unit for flowrate

KESAN GABUNGAN RAWATAN ASID TERHADAP PENGHASILAN SILICON CARBIDE (SiC) DARIPADA JERAMI PADI

ABSTRAK

Jerami padi adalah hasil sampingan dalam industri pertanian yang mudah didapati. Daripada hasil kajian ini, dapat disimpulkan bahawa bahan pendahulu (prekursor) silikon karbida boleh dihasilkan dengan kaedah pirolisis pada 1100°C, selama 82.65 minit dan pada kadar alir gas nitrogen sebanyak 2.00 L/min. Proses ini mampu untuk menghasilkan lebih kurang 96.45% precursor SiC daripada jerami. Prekursor SiC ini dihasilkan tanpa menggunakan sebarang pemangkin tambahan sekaligus dapat mengurangkan kos penghasilan produk. Parameter yang penting untuk penghasilan prekursor SiC ini adalah tempoh proses penghasilan dan juga kadar alir gas nitrogen. Hasil penyelidikan ini memberi kesan terhadap mengurangkan kos penghasilan SiC. Sebahagian daripada kandungan jerami padi adalah terdiri daripada bahan tidak organik yang mempunyai peratusan tinggi seperti, SiO₂, S₂O₃, K₂O, CaO, TiO₂, MnO, Fe₂O₃, CuO, ZnO dan Cl. Walaubagaimanapun, setelah diberi rawatan asid ataupun ulangan rawatan asid yg berlainan, bahan-bahan tidak organik tersebut dapat dikurangkan atau disingkirkan sekaligus. Bagi rawatan HCl, di mana asid HCl adalah asid yang paling sering digunapakai untuk penghasilan SiC hanya memberikan nilai peratus 54.3% sahaja untuk SiO₂ jika dibandingkan dengan rawatan asid yang lain. Bagi rawatan asid H₂SO₄, SiO₂ yang terhasil adalah pada kadar 65.8%. Nilai ini lebih tinggi daripada rawatan HCl, tetapi jika dibandingkan dengan asid sitrik, keberkesanan H₂SO₄ adalah kurang kerana sitrik asid menghasilkan lebih banyak SiO₂ dimana nilai nya adalah 81%. Tetapi nilai Fe₂O₃ masih tinggi. Fe₂O₃ adalah bahan tidak organik yang tidak diperlukan kerana ia boleh merencatkan proses dan juga penghasilan SiO₂. Berbeza dengan rawatan ulangan asid yang berbeza, dimana peratus Fe₂O₃ dapat dikurangkan dan juga telah menyingkirkan bahan tidak organik iaitu ZnO dan CuO dan pada masa yang sama juga asid sitrik boleh dijadikan sebagai pilihan kedua untuk penghasilan SiC. Berdasarkan proses mengurangkan, mendapati bahawa rawatan asid membantu dalam mengurangkan peratus bahan tidak organik yang terkandung dalam bahan mentah yang tidak tulen dengan mempunyai struktur yang porous seperti yang disahkan melalui proses analisa FTIR. Hasil pencirian juga menunjukkan berkemungkinan hasil dalam penyediaan SiC terdiri daripada terbentuknya hablur dan rambut halus SiC adalah melalui proses pirolisis. Dengan ini dapat dipastikan bahawa rawatan asid ulangan (CATS) mempunyai potensi yang tinggi dalam penghasilan SiC diaman ketulenan telah pun dapat dikenalpasti dan menyamai moissanite-3C dan digunakan dalam industri.

THE EFFECT COMBINATION OF ACID TREATMENTS FOR SILICON CARBIDE (SiC) PRODUCTION FROM RICE STRAW

ABSTRACT

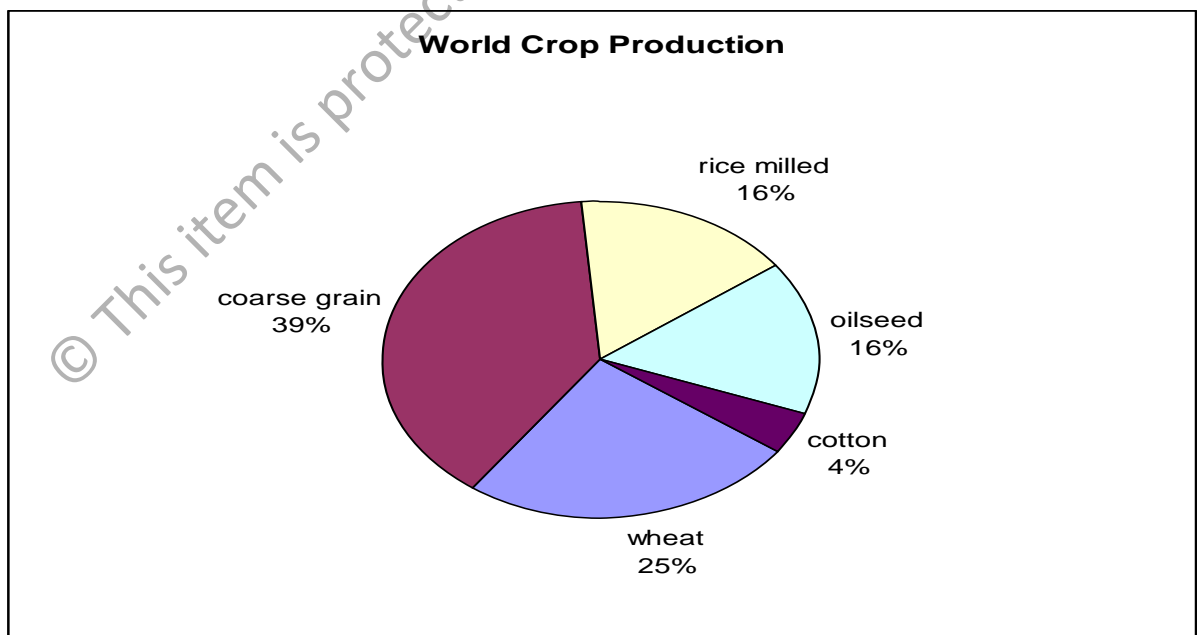
Rice straw is an abundant and low cost agricultural waste with is locally available. On the basis of this study, it is concluded that 96.45 % silicon carbide pre-cursor can be produced by the process of pyrolysis of rice straw at 1100 °C with a holding time of 82.65 minutes and a flow rate of 2.00 L/min nitrogen. The SiC pre-cursor was produced without additional catalyst process, thus which can reduce the cost of the product. The most significant parameter that contributes to the highest yield of SiC pre-cursor is the holding time and the nitrogen flowrate. This outcome is important because of the short pyrolysis time and at low temperature will result in reduced manufacturing costs. The rice straw itself have a high percentage of inorganic compound material; which is SiO₂, SO₃, K₂O, CaO, TiO₂, MnO, Fe₂O₃, CuO, ZnO, Cl compared to the other acid treated samples and consecutive acid treated (CATS) samples. With the removal some of the inorganic compound such as ZnO and CuO will increase the percentage of the SiO₂ produced. In the HCl acid treated samples which are a commonly used acid for the SiC production produce only SiO₂ at 54.3 % compared to other treatments. In the H₂SO₄ acid treated samples, the SiO₂ yield is at 65.8 % which is higher than HCl sample which can be believed it can be the choice of impurities removal but when compared to the citric acid (C₆H₈O₇) the efficiency of sulphuric acid (H₂SO₄) are low because in the C₆H₈O₇ the SiO₂ percentage is the highest which is at 81 % but have the highest percentage of 2.98% Fe₂O₃. The Fe₂O₃ is an unwanted inorganic compound because the Fe₂O₃ can inhibit the process of SiC production thus, resulting the lower production value and SiO₂. The consecutive acid treatment giving the essential result to produce SiC which is having the lowest value of Fe₂O₃ and also eliminate the ZnO and CuO and the C₆H₈O₇ acid treated sample can be the second option to produce the SiC respectively. Regarding to leaching process it was found that acid treatment helped to reduce the level of inorganic compound, leading to higher purity of raw material with porous structure as confirm in FTIR analysis. The characterization results showed the possibility for production of silicon carbide with well-developed whiskers and crystal structure from rice straw by pyrolysis process in this experiment. With these it confirms that the CATS have a higher potential in SiC production with purity were found to be comparable to a moissanite -3C and acceptable in the market.

CHAPTER 1

INTRODUCTION

1.1 Agricultural residue

Agriculture (a term, which encompasses farming) is the process of producing food, feed, fibre, and other goods by the systematic raising of plant and animal. According to the Statistical Data Food and Agriculture Organization (FAOSTAT), the world annual paddy production is approximately 582 million tons. *Oryza sativa L.* husks (Rice husk) comprise 25 mass % of the rice grain and therefore, 145 million tons of rice husk residue are produced (Genieva, et al. 2008). The total world productions of crop are nearly 3277 million matrices ton per year, among the crops are rice, wheat, sugar cane, maize and many others are illustrate in Figure 1.1.



Source: Production Estimates and Crop Assessment Division, FAS, USDA, 2004.

Figure 1.1

World crop production (USDA, 2004)

In the agricultural, the resources are mostly renewable, widely distributed, available locally, mouldable, anisotropic, hydroscopic, recyclable, versatile, non-abrasive, porous, viscoelastic, easily available in many forms, biodegradable, combustible, compostable and reactive (Rowell et al., 2000). On the other hand, agriculture also produces a lot of residue and the agricultural residue is the waste that comes from any farming activities or agro-industry such as crops harvesting, abattoirs and tanneries. These residue or waste includes organic sludge effluents, unused pesticides and fertilizer, chemical container and crop residue. Waste is often defined as something unwanted and has no economic value.

However, increasingly waste generation may provide a source with certain economic values for another usage. Whereas new products can be generated from various kinds of crop residues with appropriate technology, for examples generation of energy from palm oil waste, production of compost or fertilizer from rice husk and converting rice husk to carbon and etc. Furthermore, waste if not handled properly will effect to human health and the environment (IMPAK, 2006).

1.2 Paddy

'Paddy' is one of the agriculture crops. The word "paddy" is derived from the Malay word '*padi*' (rice plant). Rice is a cereal foodstuff which forms an important part of the diet for many people worldwide. Domesticated rice comprises two species of food crops in the Poaceae ("true grass") family, *Oryza sativa* (Asian rice) and *Oryza glaberrima* (African rice)

These plants are native to tropical and subtropical southern Asia and southeastern Africa (Crawford and Shen, 1998). The plant has many different variations, but is generally a short living plant, with an average life span of 3-7 months, depending on the climate and the variety in certain country. It is not a water plant but substantial amounts of water are required for the planting. Cultivated species of rice are considered to be semi-aquatic annuals. The height of the plant can range from 0.4 m to over 2 m. The botanical features of paddy or rice plant example the leaf blade, leaf sheath and stem are shown in Figure 1.2.

Nowadays, the world production of rice has risen steadily from about 200 million tons of paddy rice in 1960 to 600 million tons in 2004 (FAOSTAT, Research Institute Statistic, 2004). Milled rice is about 68% of paddy rice by weight, Figure 1.3 show that the top three producers of rice were China (26% of world production), India (20%), and Indonesia (9%) according to Statistical Data Food and Agriculture Organization FAOSTAT in year 2008. Rice is the world's second largest cereal crop after wheat but in the other hand produce the largest amount of crops residue, about 330 million metric tons and 90% of the world's production is in developing countries of East and Southeast. Specifically in Malaysia, the paddy production in 2007 are 2,375,000 tons and in 2008 are 2,385,000 tons, and the productions of rice parallel to paddy production in 2007 are 1,531,000 tons for 2008 are 1,535,000 tons are shown in Table 1.1 (MADA, 2008). According to USDA, Foreign Agriculture Department Service, Malaysian rice productions crop area from year 2007/08 until 2009/10 is increasing to 1.98 million hectares.

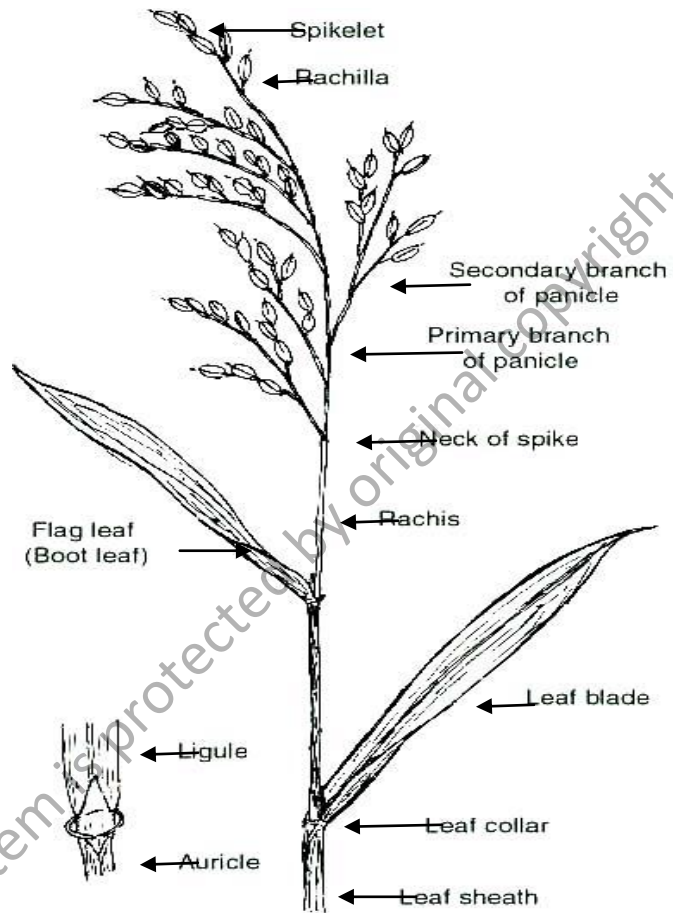
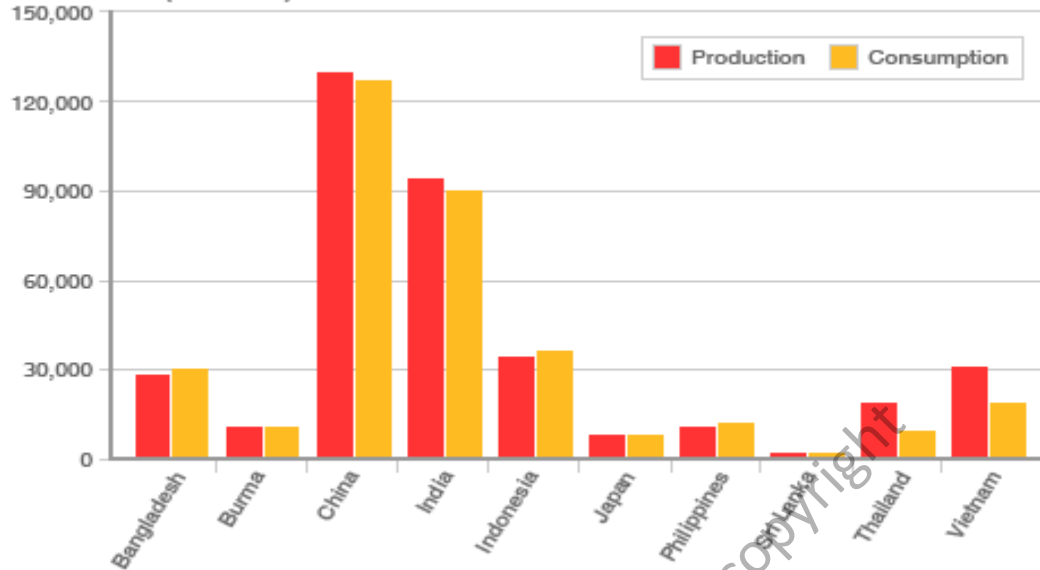


Figure 1.2 :

Name of rice panicle parts (Armstrong, 2003)

RICE PRODUCTION AND CONSUMPTION

Metric tonnes (thousands)



Note: figures for milled rice for year ending March 2008
Source: USDA-FAS, Production, Supply and Distribution (PS&D) database

SOURCE: USDA

Figure 1.3 :

Productions and consumption of rice for the South Asian countries in 2008 (FAO, 2008)

Table 1.1: Malaysian production of paddy and rice (MADA, 2008).

Item	2007	2008
Paddy parcels area (hectareage)	426,224	426,260
Planted paddy area (hectareage)	676,111	670,524
Paddy production ('000 tonnes)	2375	2384
Production values (RM)	1,543,750	1,788,000
Rice production ('000 tonnes)	1,531	1,535
Average yield of paddy (Kg/Ha)	3,514	3,556
Total rice import ('000 tonnes)	798.70	657.90

Source: Department of Agriculture, Malaysia MADA.

(FOA, 2006) Asian countries are main production country of rice as rice is the main source of food for Asian. The temperature regime and the rainfall distribution in the Malaysia are suitable for year round cultivation of rice, even under rain fed conditions. Therefore, the rice has been commercially planted in Malaysia. About 300,500 hectares on Malaysia Peninsular and 190,000 hectares on Borneo Islands are devoted to rice production (MADA, 2008).

1.3 Rice Straw

Plate 1.1 is an agricultural residue, it is rice straw after the nutrient grain or seed has been removed. Rice straw is low in lignin and high in silica content compare with other straw (Van Soest, 2002). Straw makes up about half of the yield cereal crops such as barley, oats, rice, rye or wheat. In times gone by, it was regarded as a useful by-product of the harvest, but with the advent of the combine harvester, straw has become more burdensome to agriculture.

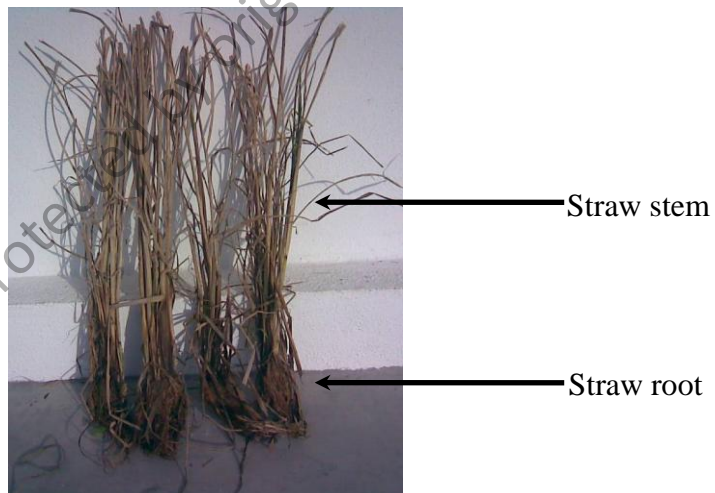


Plate 1.1

Local paddy straw (rice straw)

Rice straw is a major agricultural by product in Asia, where its annual production amounts to 350 million tons which is 90 % of world total production (Han and Anderson, 1974). Recently, the straw is used as roofing and packing material, feed, fertilizer, and fuel. These uses however are minor and will soon end as advanced economics and technology make them unprofitable. In the United States, rice straw has