

## OPTIMIZATION AND REACTIVITY STUDY OF SILICA IN THE SYNTHESIS OF ZEOLITES FROM RICE HUSK

ZAINAB RAMLI  
ENDANG LISTIORINI

&

HALIMATON HAMDAN

Department of Chemistry

Faculty of Science

Universiti Teknologi Malaysia

Karung Berkunci 791

80990 Johor Darul Ta'zim

Malaysia

**Abstract.** Although the chemical extraction of silica from rice husk ash (RHA) is well established; its reactivity in the synthesis of zeolites have not been studied and optimized. Due to the complex nature of silica, the extraction procedure is important in ensuring production of highly reactive silica. This paper reports on the optimization of the extraction procedure and determination of the factors that influence impurities are the factors that influence the reactivity of silica. Pure amorphous silica was obtained with RHA:NaOH ratio of  $\leq 1.5$  and sodium silicate concentration (measured in specific gravity) of 1.2-1.5. Reactivity rests of the extracted silica via crystallization of zeolite Y in reaction mixtures of various basicity show that pure zeolite Y was formed from the sample containing  $\geq 85\%$  SiO<sub>2</sub> with neutral or slightly basic property. In contrast, crystallization in the presence of silica source that is acidic containing a low percentage of SiO<sub>2</sub> favours the formation of zeolite P.

### 1.0 INTRODUCTION

Several types of zeolites have been synthesized successfully using silica and alumina from natural resources, (Yashida and Inove [1], Bajpai, Gokhale and Roa [2], Dalal, Roa and Gokhale [3], Rawtani, Roa and Gokhale [4] & Chen and Yeoh [5]). The natural resources are normally volcanic ash and minerals such as metakaolinite; an amorphous silica-aluminate clay. However, the use of these resources in the synthesis of zeolites are rather limited due to the presence of impurities.

In Malaysia, rice husk ash is produced in abundance after every rice harvesting season. Silica is the major constituent of rice husk. Silica ash which is transformed from the husk by complete burning constitutes 15-20% of the total weight of the husk, The silica ash that is produced contains  $>90\%$  SiO<sub>2</sub>. Because of its nonbiodegradable property, the presence of the silica ash causes a number of problems to the environment. In order to solve these problems, useful applications of the waste product are desirable.

Synthesis of a few types of zeolites from rice husk have been reported (Bajpai, Gokhale and Roa [2], Dalal, Roa and Gokhale [3], Rawtani, Roa and Gokhale [4] & Chen and Yeoh [5]). However, there has been no report on an established procedure on the extraction of

silica from the rice husk. Considering that rice husk ash contains a high percentage of silica, it is therefore an interest to establish an optimized extraction procedure and study the reactivity of the silica obtained from the rice husk in the synthesis of zeolites. This paper reports on a systematic study of the chemical extraction of silica from the local rice husk ash which focuses on the optimization procedure, followed by reactivity testing via the synthesis of zeolite Y.

## 2.0 EXPERIMENTAL

### 2.1 Preparation of Materials

The rice husk ash used as the starting material was taken from Bagan Serai, Perak. Aluminium hydroxide (Radel de Haen, 70% w/w  $\text{Al}_2\text{O}_3$ , 30% w/w  $\text{H}_2\text{O}$ ), sodium hydroxide (Radel de Hean, 99%),  $\text{H}_2\text{SO}_4$  (Koch Light, 98%), were directly used without purification. Distilled water was used in the synthesis, preparation of solution and washing in order to minimize the introduction of impurities.

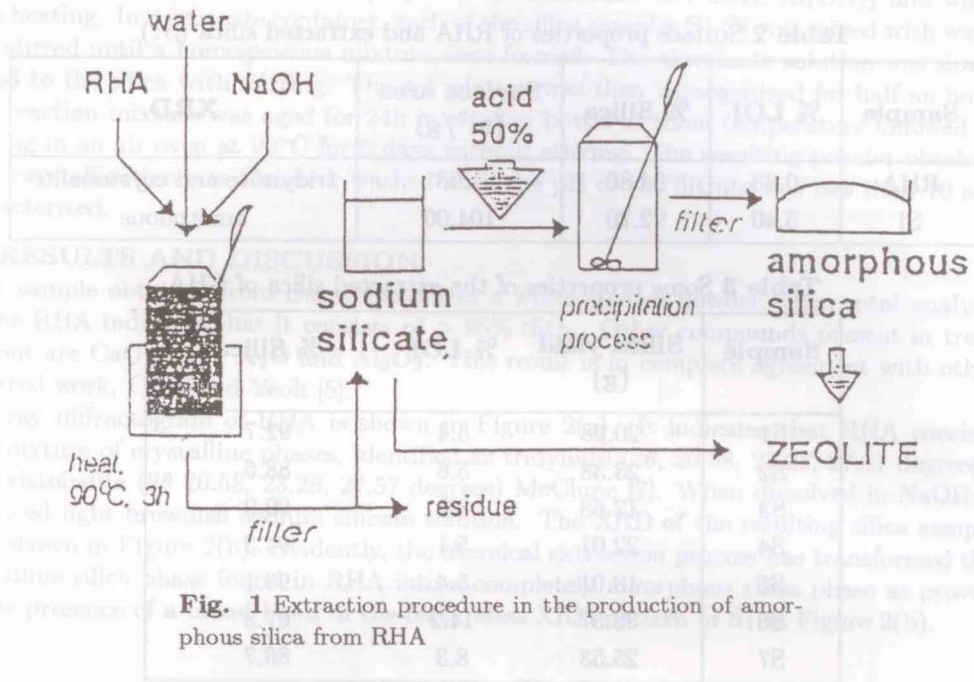
### 2.2 Chemical Extraction of Amorphous Silica From Rice Husk Ash (RHA)

The chemical extraction of silica was carried out based on established procedure, Chen and Yeoh [5]. The initial stage involves the formation of sodium silicate; achieved by mixing RHA with aqueous NaOH of various ratios and heated at  $90^\circ\text{C}$  with stirring for 3h. The resulting sodium silicate solution was filtered and the residue was washed several times with deionised water. The density of the resulting solution was measured using the density hydrometer. In order to keep the concentration of the filtrate having a specific gravity value of 1.120–1.130 as suggested by earlier work, Chen and Yeoh [5], the filtrate was either diluted with water or concentrated by heating.

Precipitation of silica was carried out by neutralization of the resulting sodium silicate solution with 50% w/w concentration of sulphuric acid solution. The sulphuric acid was slowly added to the sodium silicate solution with stirring and monitoring of the pH. A gel like silica precipitate thickened immediately when the pH of the mixture approached 10.5. At this point, the addition of sulphuric acid was further added into the gel mixture until it became neutral. The resulting silica was washed several times with water, filtered and dried at  $110^\circ\text{C}$ . The extraction procedure is illustrated in **Figure 1**.

All silica samples S1-S7 are amorphous to XRD. However, each of the IR spectra of samples S3 and S6 exhibits a significant band at wavenumber  $618\text{ cm}^{-1}$  which corresponds to a crystalline silica phase namely cristobalite. The silica yield and some physical properties of samples S1-S7 are given in Table 3. The results indicate that for the same amount of RHA used, the yield of product strongly depends on the amount of NaOH as demonstrated in samples S2 and S3. NaOH increases the dissolution of silica from RHA into the sodium silicate solution. Consequently, more silica was precipitated from such solution. The lowest yield of silica product was in sample S3 which was extracted in comparatively the lowest amount of NaOH.





**Fig. 1** Extraction procedure in the production of amorphous silica from RHA

**Table 1** Chemical compositions and characteristics of reactants in the production of amorphous silica

Samples	Ash (g)	NaOH (g)	Final Volume Of sodium silicate solution (ml)	Sodium silicate (s.g)	H <sub>2</sub> SO <sub>4</sub> (%v/v)	Final pH
S1	30	20	253	1.125	50	8.34
S2	30	25	298	1.124	50	7.63
S3	30	15	200	1.122	50	3.50
S4	30	20	257	1.122	75	7.70
S5	30	20	247	1.124	25	7.42
S6	30	20	270	1.100	50	6.59
S7	30	20	200	1.150	50	7.70

Note: s.g.: specific gravity

**Table 2** Surface properties of RHA and extracted silica (S1)

Sample	% LOI	% Silica	Surface area (m <sup>2</sup> /g)	XRD
RHA	0.83	94.80	1.63	tridymite and cristobalite
SI	5.40	92.70	104.00	amorphous

**Table 3** Some properties of the extracted silica of RHA

Sample	Silica yield (g)	% LOI	% Silica
S1	20.98	5.4	92.7
S2	23.38	5.6	88.6
S3	17.68	8.0	90.0
S4	22.01	5.1	94.3
S5	18.01	5.4	96.1
S6	32.57	14.2	67.8
S7	25.53	8.3	86.7

Sulphuric acid is the precipitating agent of silica. The concentration of H<sub>2</sub>SO<sub>4</sub> in general determines the ease of precipitation without appreciable influence on the yield of the silica produced. However, the quality of the resulting amorphous silica greatly depends on the technique of precipitation. The addition of acid to the sodium silicate solution encountered a problem once the precipitate-like gel started to form as the pH of the mixture approached 10.5. At this point, the mixture had to be mixed thoroughly in order to avoid the accumulation of low pH areas in the mixture which favours the formation of silica particle aggregates, Chen and Yeoh [5]. In the presence of such aggregates, it was difficult to achieve the neutralization point due to the pH gradient created in the unhomogeneous mixture. Failure to control the formation of silica aggregates caused overshooting of the neutralization point as observed in sample S3 where the final pH of the mixtures was 3.5 making it acidic.

An important parameter in producing silica with high yield is the concentration of the resulting sodium silicate solution prior to the precipitation of silica. Sample S1-S5 and S7, precipitated from sodium silicate solutions of higher concentrations contain more than 85% silica. In order to optimize the extraction parameters, the NaOH:SiO<sub>2</sub> ratios and H<sub>2</sub>SO<sub>4</sub> used in the neutralization were varied while keeping the amount of water constant. Table 1 lists the parameters used for each extraction process. The silica samples which resulted from these extraction processes are labelled as S1-S7.

### 2.3 Synthesis of Zeolite Y

Zeolite Y was synthesized using the extracted silica samples S1-S7. Two different reaction mixtures of the following compositions were used (Chen and Yeoh [5], Halimaton [6]):

Composition A: 2.24 Na<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> : 8 SiO<sub>2</sub> : 112 H<sub>2</sub>O

Composition B : 7.30 Na<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> : 18 SiO<sub>2</sub> : 300 H<sub>2</sub>O



Sodium aluminate solution was prepared by dissolution of NaOH,  $\text{Al}(\text{OH})_3$  and water with heating. In a separate container, each of the silica samples S1-S7 was mixed with water and stirred until a homogeneous mixture were formed. The aluminate solution was slowly added to the silica with stirring. The gel mixture was then homogenized for half an hour. The reaction mixture was aged for 24h in a teflon bottle at room temperature followed by heating in an air oven at  $90^\circ\text{C}$  for 6 days without stirring. The resulting powder obtained after crystallization was filtered, washed until the pH of the filtrate was less than 10 and characterized.

### 3.0 RESULTS AND DISCUSSION

RHA sample obtained from Bagan Serai was a white-pinkish powder. Elemental analysis on the RHA indicates that it consists of  $> 95\%$   $\text{SiO}_2$ . Other compounds present in trace amount are CaO, MgO,  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ . This result is in complete agreement with other reported work, Chen and Yeoh [5].

X-ray diffractogram of RHA is shown in Figure 2(a). It indicates that RHA consists of a mixture of crystalline phases, identified as tridymite ( $2\theta$ , 20.58, 23.28, 27.57 degrees), and cristobalite ( $2\theta$  20.58, 23.28, 27.57 degrees) McClune [7]. When dissolved in NaOH it produced light brownish sodium silicate solution. The XRD of the resulting silica sample S1 is shown in Figure 2(b). Evidently, the chemical extraction process has transformed the crystalline silica phase found in RHA into a completely amorphous silica phase as proven by the presence of a broad band in the featureless XRD pattern of S1 in Figure 2(b).

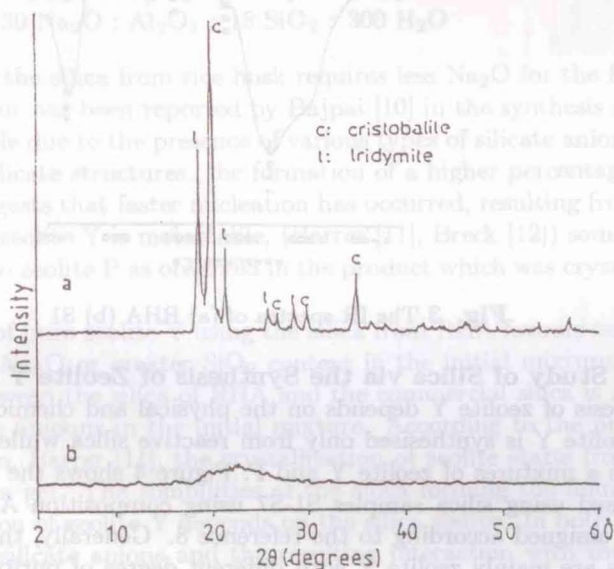


Fig. 2 The XRD of (a) RHA (b) S1

The IR spectra of RHA and S1 are shown in Figure 3. Both samples exhibit very strong bands at wave numbers  $1100\text{ cm}^{-1}$ ,  $798\text{ cm}^{-1}$  and  $460\text{--}480\text{ cm}^{-1}$  which correspond to asymmetric stretching of tetrahedral  $\text{SiO}_4$ , symmetric stretching of  $\text{SiO}_4$  tetrahedra and

T-O bending band vibrations, respectively. The IR spectrum of RHA sample in Figure 3(a) is identical to tridymite with an additional band at  $622\text{ cm}^{-1}$  indicating the presence of the cristobalite phase, Willis, der Mas & Miller [8]. This observation supports the results obtained from XRD studies. The IR spectrum of the silica sample S1 is also similar to that of tridymite but it exhibits an additional band at  $962\text{ cm}^{-1}$ ; which is assigned to SiOH groups, typical of the silica gel phase, Willis, der Mas & Miller [8].

Table 2 represents the surface properties of RHA and S1. The % loss of ignition (LOI) value increases markedly in sample S1 due to the loss of silanol groups; found in abundance in S1, as water at  $1000^\circ\text{C}$ . Such loss naturally affects the silica content of sample S1. However, the surface area of sample S1 was greatly enhanced compared to RHA as a direct consequences of S1 being amorphous.

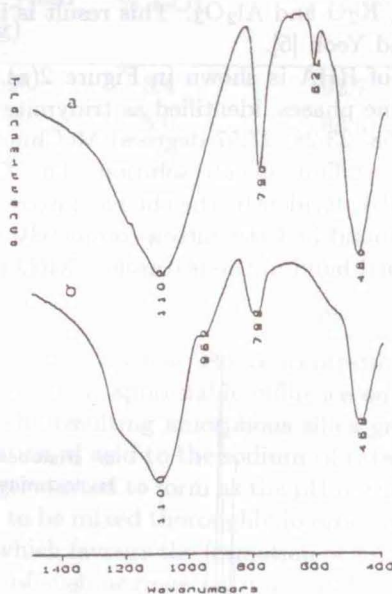


Fig. 3 The IR spectra of (a) RHA (b) S1

### 3.1 Reactivity Study of Silica via the Synthesis of Zeolite Y

Successful synthesis of zeolite Y depends on the physical and chemical state of the amorphous silica. Zeolite Y is synthesised only from reactive silica while the unreactive silica usually produces a mixture of zeolite Y and P. Figure 4 shows the XRD patterns of the zeolites synthesised using silica samples S1-S7 using composition A and B, respectively. The peaks were assigned according to the reference 8. Generally, the XRD data indicate that the samples are mainly zeolite Y with different degree of purity. Table 4 represents the purity and crystallinity of zeolite Y formed from the silica sources S1-S7. The results show that by using both composition mixtures, silica samples S1, S4 and S5 produced pure zeolite Y, whereas silica samples S2, S3 and S6 produced a mixture of zeolite Y and P.

The successful formation of zeolite Y from silica S1-S7 (except S3) indicate that crystallization of zeolite Y favours neutral or slightly basic environment (Table 3 and 4). In contrast, preparation of zeolite Y from the acidic sample S3 produced zeolite P instead of



zeolite Y (Figures 4I(c) and 4II(c)). Samples S2, S6 and S7 also produced zeolite P in addition to zeolite Y which suggest that these silica samples might contain isolated aggregates of acidic silica powder. Pure and highly crystalline zeolite Y was produced from the reaction mixture A; with a lower alkalinity than mixture B as shown in Table 4.

Table 4 Synthesis of zeolite Y from the silica extracted from Table 1

Silica Sample	Composition A		Composition B	
		% Crystallinity		% Crystallinity
1	Y	100	Y	76
2	Y	88	Y+P	67
3	Y+P	17	P	
4	Y	96	Y	96
5	Y	89	Y	88
6	Y+P	74	Y+P	83
7	Y	96	Y+P	81

Note: P : Zeolite P; Y : Zeolite Y

Composition A:  $2.24 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 8 \text{ SiO}_2 : 112 \text{ H}_2\text{O}$

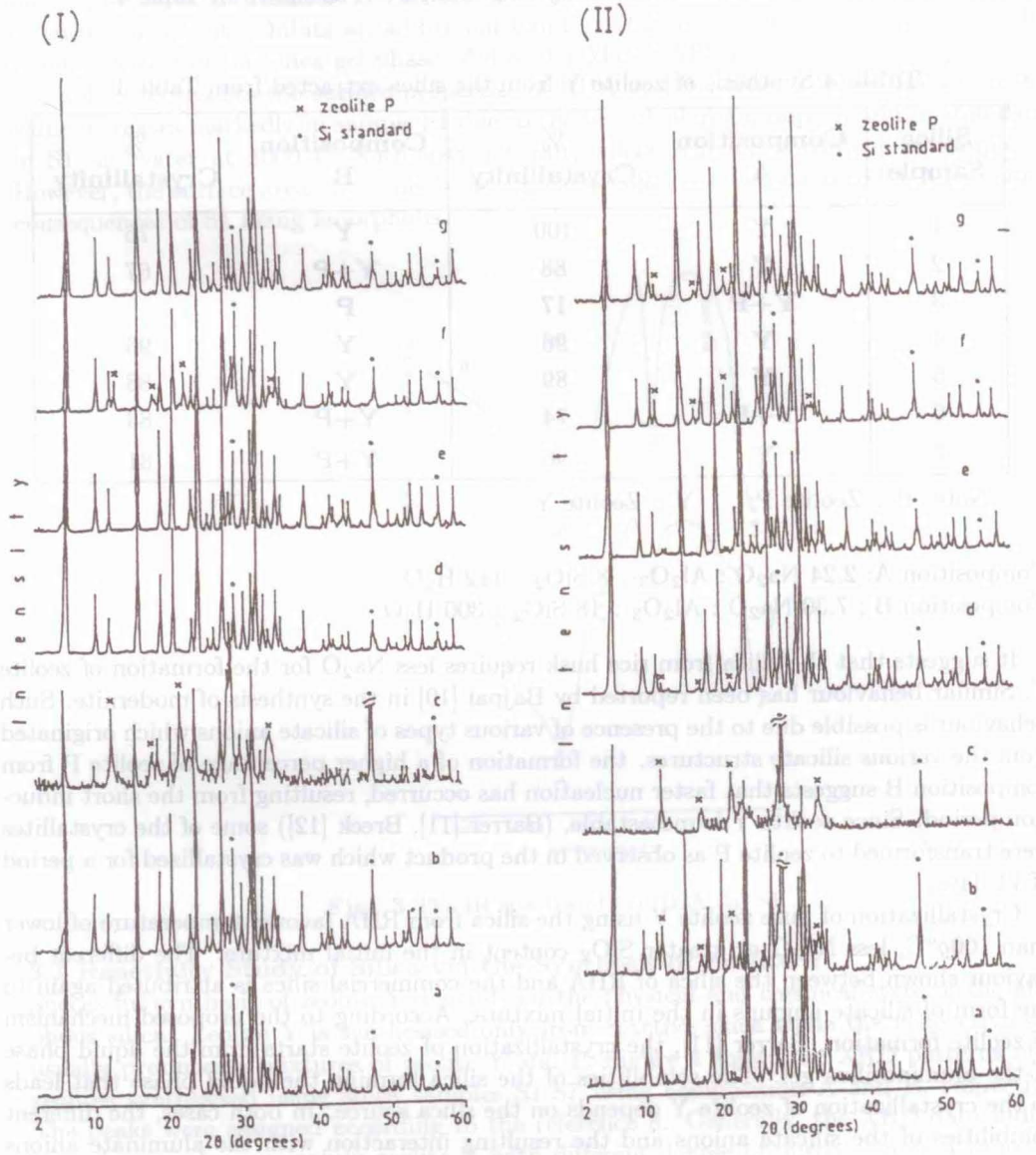
Composition B:  $7.30 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 18 \text{ SiO}_2 : 300 \text{ H}_2\text{O}$

It suggests that the silica from rice husk requires less  $\text{Na}_2\text{O}$  for the formation of zeolite Y. Similar behaviour has been reported by Bajpai [10] in the synthesis of modernite. Such behaviour is possible due to the presence of various types of silicate anions which originated from the various silicate structures. The formation of a higher percentage of zeolite P from composition B suggests that faster nucleation has occurred, resulting from the short induction period. Since zeolite Y is metastable, (Barrer [11], Breck [12]) some of the crystallites were transformed to zeolite P as observed in the product which was crystallized for a period of 14 days.

Crystallization of pure zeolite Y using the silica from RHA favours temperature of lower than  $100^\circ\text{C}$ , less  $\text{Na}_2\text{O}$  or greater  $\text{SiO}_2$  content in the initial mixture. The different behaviour shown between the silica of RHA and the commercial silica is attributed again to the form of silicate anions in the initial mixture. According to the proposed mechanism of zeolite formation, Barrer [11], the crystallization of zeolite starts from the liquid phase of the aluminosilica gel. The solubilities of the silica forming the liquid phase that leads to the crystallization of zeolite Y depends on the silica source. In both cases, the different solubilities of the silicate anions and the resulting interaction with the aluminate anions presence in the solution contributes to the different behaviour of both types of silica.

#### 4.0 CONCLUSION

Successful synthesis of zeolite Y depends on the reactivity of the silica source when other reactants and parameters are kept constant. Chemical extraction of RHA transformed the crystalline silica phase initially present to an amorphous silica phase. The amorphous



**Fig. 4** The XRD of zeolite Y crystallized from composition A (I) and composition B (II) using samples (a) S1 (b) S2 (c) S3 (d) S4 (e) S5 (f) S6 (g) S7 as silica source



silica extracted from RHA is reactive towards the synthesis of pure zeolite Y. In conclusion, the study has shown that the extracted silica from RHA is active when it is completely amorphous, has high surface area and slightly basic. The presence of acidic silica favours the formation of zeolite P. Extraction of silica by physical means has been carried out and comparative study on its reactivity with that obtained in this study will be reported elsewhere.

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## PENGENALAN

Keberhasilan penyelesaian kamiran lintasan bagi penamaan resapan linear tertitik dalam bentuk satu berbentuk:

$$\psi_1(x, t) = \alpha \psi_{11}(x, t) - \beta V(x, t) \psi(x, t), \quad \psi(x, 0) = \phi(x) \quad (1)$$

di mana  $\alpha, \beta$  adalah pemalar kompleks yang sesuai (nilai tertentu  $\alpha$  dan  $\beta$  memberikan penyelesaian haba atau Schrödinger) dan subskrip merandakan terbitan separa, telah dipostulatkan dahulu oleh Feynman [2] bagi kasus  $\alpha = \hbar/2m$  dan  $\beta = \hbar/\lambda$  (nilai pemalar Schrödinger bagi arah berjalan  $\lambda$ ,  $2\pi\hbar = h$  pemalar Planck). Kini penyelesaian kamiran lintasan itu terkenal sebagai 'kamiran Feynman'.

$$\psi(x, t) = \int \exp\left\{i(t/\hbar) \int_0^x [(m/2)\dot{\gamma}^2(s) - V(\gamma(s))]\, ds\right\} \phi(\gamma(0)) \, d\gamma. \quad (2)$$

'Kamiran' dilakukan ke atas semua lintasan klasik  $\gamma(s)$  yang memenuhi  $m\dot{\gamma}^2 = (2V/\phi\gamma)$  dengan  $\gamma(0) = x$  (ini merandakan terbitan terhadap  $x$ ). Walau bagaimanapun, resapan kini 'kamiran Feynman' itu masih memiliki kecacatan radikal di segi justifikasi matematikanya (Hooft [7]), khususnya berkaitan 'salatan kuantum'nya. Semenjak Feynman dan ramai penyelidik cuba memformulasi berbagai-bagai pendekatan rapi bagi menaktubkan penyelesaian kamiran tersebut, walaupun umum menyetujui bahawa formula-formulasi tersebut masih terasah daripada hipotesis Feynman itu (Shaharir [11]) untuk perbincangan lanjut. Walau bagaimanapun, bagi kasus  $\alpha > 0$  dan  $\beta > 0$  (persamaan haba atau resapan