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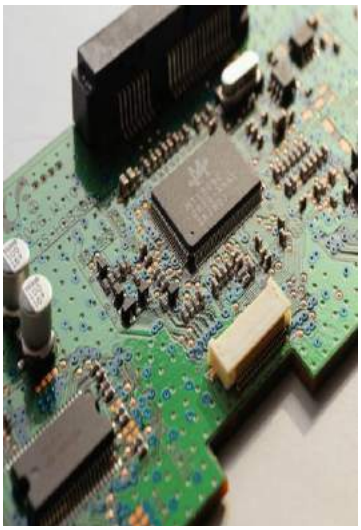


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Content

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An Advance Approach of Image Encryption using AES, Genetic Algorithm and RSA Algorithm

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***Abstract*— In current scenario the entire world is moving towards digital communication for fast and better communication. But in this a problem rises with security i.e. when we have to store information (either data or image) at any casual location or transmit information through internet. As internet is an open transmission medium, security of data becomes very important. To defend our information from piracy or from hacking we use a technique and i.e. known as Encryption Technique. In this paper, we use image as information and use an advance approach of well-known encryption techniques like AES, Genetic Algorithm, and RSA algorithm to encrypt it and keep our information safe from hackers or intruders making it highly difficult and time consuming to decipher the image without using the key.**

Keywords-AES, Communication, Decrptyion, Encryption, Genetic, Information, Open Transmission Medium, RSA, Security.

I. INTRODUCTION

In recent scenario information or data transmission is done through electronic means or we can say with the help of internet. Internet is an open transmission medium, so there is chance of data hacking or data piracy while it is being transmitted. Another problem arises with the data storage. That is sometimes we save some crucial messages in such devices which are operated by many people. So, at that time there is chance of Piracy of data. To stop these all piracy and hacking a technique is used to protect our information and is known as Encryption Technique. Encryption is a technique which uses finite set of instructions called an algorithm [1] to convert original message known as plain text, into encrypted form (or coded form) known as cipher text. Cryptographic algorithm normally requires a set of characters called as 'key' to encrypt or decrypt data. With the help of key and algorithm we can encrypt or decrypt plain text into cipher text and then cipher text to plain text.

Encryption is of two types. One is Asymmetric Algorithm which is also called Asymmetric cryptography. It is usually implemented by the use of one-way functions. In mathematical terms, these are functions that are easy to compute in one direction but very difficult to compute in reverse manner. This is what allows you to publish your public key, which is derived from your private key. A common one-way function used today is factoring large prime numbers. It is easy to multiply two prime numbers together and get a product. However, to find out the factors there are numerous possibilities, and it is one of the great mathematical difficulties e.g. RSA Algorithm

And second one is Symmetric Algorithm which is also called as called symmetric cryptography or shared secret encryption [2]. This form of encryption uses a secret key, called the shared secret, to mix up the data into impenetrable twaddle. The person on the receiver end needs the shared secret (key) to unlock the message. It is called symmetric cryptography because the same key is used on both ends (i.e. at the sender end and at receiver end) for both encryption and decryption e.g. Genetic Algorithm.

In this paper, we take an image as input and perform different encryption technique over it. Here we encrypt a single image with three different encryption techniques [3] one by one in which some techniques are of symmetric algorithm and some are of asymmetric algorithm (like Genetic, AES, and RSA). Here all encryption techniques are used one by one that is output of one encryption technique is converted in input, of another encryption technique, or it is better to say all encryption technique is used in cascade manner. After execution of all encryption technique over input image, we get a highly encrypted image which is very difficult to decrypt without the authorization of its generator because of its dual nature i.e. symmetric and asymmetric encryption technique. Here to decrypt the image users need 'key', because of secret key algorithm, and the key must be provided by generator only.

II. METHODOLOGY

Here a list of the several encryption techniques are given which are used in this hybrid model of image encryption technique.

A. AES Algorithm

It is also known as Rijndael [2]. The AES algorithm [7] was developed by Vincent Rijmen and Joan Daemen. In October 2000 NIST acknowledged that AES algorithm is one of best algorithm in security, performance, efficiency, ability

of implementation, and also flexibility. The AES is a symmetric key algorithm, in this both sender and receiver uses identical key to encrypt data into cipher and then to decrypt cipher into original data. In this algorithm, it has a fixed block length of 128 bits, while the length of key size can be of 128, 192, or 256 bits. It [3] is an iterative algorithm. It is composed of 4 basic operational blocks. For complete encryption iteration is performed up to N times. The total number of iteration i.e. N can be 10, 12, and 14 based on key length i.e. 128, 192, and 256 respectively.

1) Encryption: In the key expansion round keys are derived from the cipher key using Rijndael's key schedule. AES requires a separate 128-bit round key block for each round plus one more.

a) *Initial Round:* Add Round Key, each byte of the state is combined with a block of the round key using bitwise XOR.

b) *Iterative Round's:* In the iterative round four operations are performed which include sub bytes operation which is a non-linear substitution step where each byte is replaced with another according to a lookup table. Shift rows is a transposition step where the last three rows of the state are shifted cyclically a certain number of steps. Mix columns is a mixing operation which operates on the columns of the state, combining the four bytes in each column. Finally, addition of round key is performed.

c) *Final Round:* In the final round all the above operations are repeated except in the final round mix columns is not performed.

2) Decryption: Inverse sub bytes, inverse shift rows and inverse mix columns are used in reverse order instead of sub bytes, shift rows, and mix columns. The key expansion remains the same.

B. Genetic Algorithm

Genetic Algorithm (GA) is a penetrating technique used in computer science to find out approximate solution to optimization problems. Genetic Algorithm [8] (GA) is first proposed by John Holland and his contemporaries at the University of Michigan in 1975. Genetic Algorithm is a particular class of evolutionary algorithm that used techniques inspired from human evolution *or* evolutionary biology like inheritance, mutation, natural selection and recombination (also called crossover).

B. 1) Encryption: Take an image as input. Calculate its Height (H) and Width (W) of the input image [9]. Find (H mod 8) and (W mod 8), if they are equal to zero then go to next step

$$H = H + (8 - (H \bmod 8)) \quad (3)$$
$$W = W + (8 - (W \bmod 8)) \quad (4)$$

Divide input image in two blocks, each block size is of (8x8). Perform crossover operation. Perform mutation operation get an encrypted block. Repeat last two steps for each block to get an encrypted image.

2) Decryption: Take encrypted image as input. Go to encrypted block. Perform mutation operation followed by crossover operation to get decrypted block [10]. Repeat last two steps for each block to get decrypted image.

C. RSA Algorithm

RSA is an algorithm developed in 1977 by Ron Rivest, Adi Shamir, and Leonard Adleman [4]. In such a cryptosystem, the encryption key is a public one and the decryption key which is different from the encryption key is kept private. As two different keys are being used in encryption and decryption the RSA algorithm is also called as an asymmetric cryptographic algorithm [5].

The RSA algorithm consists of three major steps in encryption and decryption. The steps are as following

1) Key Generation: The RSA involves a public key and a private key. Of these two keys the public key is used for encrypting messages and can be known to everyone. The messages encrypted with the public key are decrypted using the private key. The process for key generation is as follows. First choose two distinct prime numbers p and q and then compute n = p x q where n is the modulus for the public key and the private keys. Next compute $\varphi(n) = (p - 1)(q - 1)$. Choose an integer e such that $1 < e < \varphi(n)$ and GCD $(e, \varphi(n)) = 1$. The pair (n, e) is the public key. The private key is a unique integer d obtained by solving the equation $d.e \equiv 1 \pmod{\varphi(n)}$.

2) Encryption: The RSA algorithm [6] is used here for encrypting an image. So the message text (m) is in the form of pixels lying in the range 0 to 255. The pixels are stored and operated upon in an array format. The text is encrypted using the public key (n, e) from the equation

$$C = M^e \bmod (n) \quad (1)$$

3) Decryption: The text is decrypted using the private key (n, d) from the

$$M = C^d \bmod (n) \quad (2)$$

The decrypted pixels are obtained in the array format and subsequently the decrypted image.

III. SIMULATION

The encryption is performed on two images one Lena.bmp shown in figure 1 and other Mandrill.bmp shown in figure 2 both of size 512×512

Figure 1. Test Image Lena

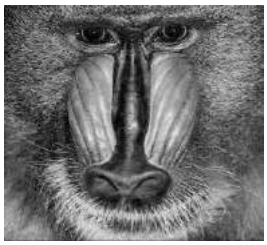

Figure 2. Test Image Mandrill

In the hybrid model, the encryption is done by combining the encryption techniques listed above in the order shown in figure 3 where the output of each technique is the input of the next encryption algorithm.

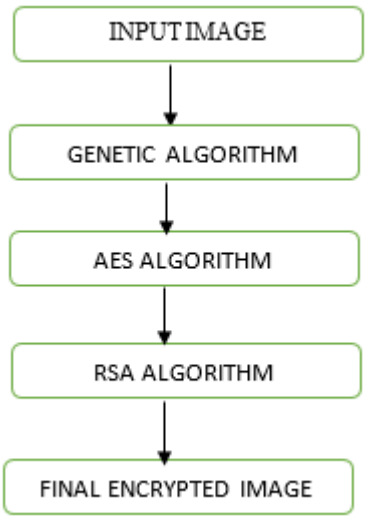

Figure 3. Flowchart for Hybrid Image Encryption

For decryption, the same techniques are applied in the reverse order shown in figure 4.

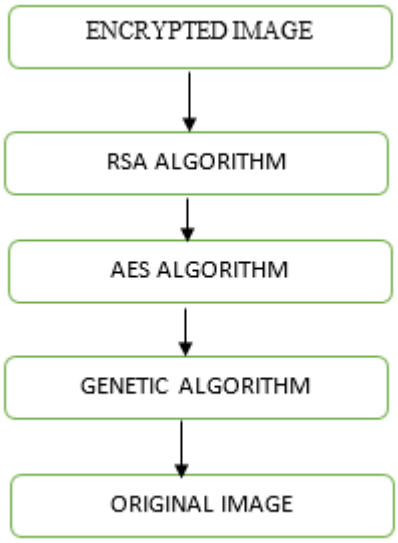

Figure 4. Flowchart for Hybrid Image Decryption

Figure 5. Test Image Lena Encryption. a) Original Image b) Genetic encryption c) AES encryption h) RSA encryption final image.

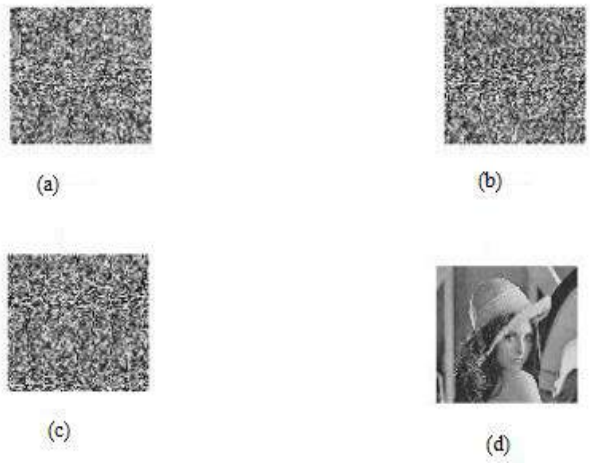

Figure 6. Test image Lena Decryption. a) RSA decryption b) AES decryption c) Genetic decryption d) original image.

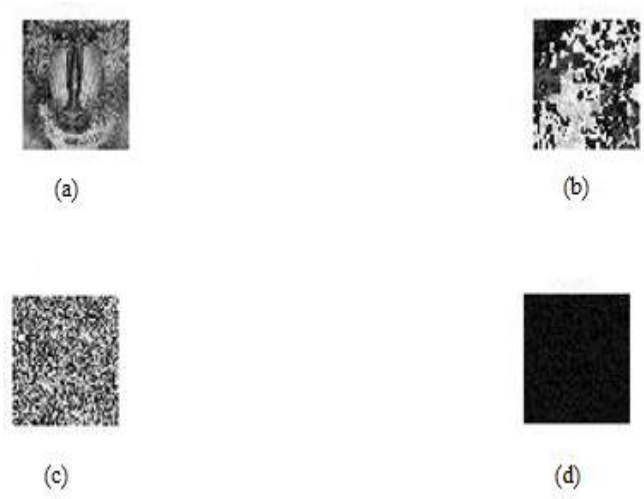

Figure 7. Test Image Mandrill Encryption. a) Original Image b) Genetic encryption c) AES encryption d) RSA encryption final image.

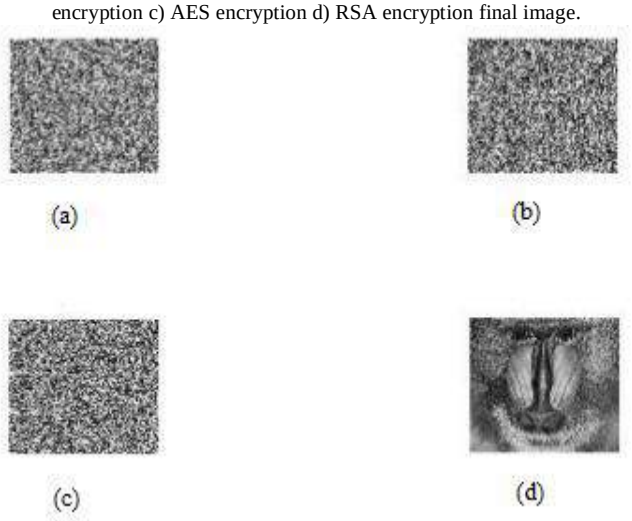

Figure 8. Test image Mandrill Decryption. a) RSA decryption b) AES decryption c) genetic decryption d) original image.

Figure 5 and 6 show the step by step encryption and decryption of the test image Lena. Figure 7 and 8 show the step by step encryption and decryption of the test image Mandrill.

IV. Measurement Parameters

To be able to tell how suitable the hybrid encryption model is the following quality measurement parameters are employed once between original image [10] and encrypted image and once between original image and decrypted image.

- Mean Square Error (MSE)
- Peak signal to Noise Ratio (PSNR)
- Normalized Absolute Error (NAE)
- Normalized cross correlation (NCC)
- Average difference (AD)
- Structural content (SC)
- Maximum difference (MD)

Table 1 shows the measurement parameters employed between the test image Lena and the encrypted Image [11] and between the original image and its decrypted image.

TABLE I. QUALITY MEASURMENT PARAMETERS FOR TESTIMAGE 1.

Measurement Parameters	**Comparison between Original Image Lena and Encrypted Image**	**Comparison between Original Image Lena and**
MSE	253.80	5.5098
AD	108.5366	1.5029
MD	243	5
NAE	0.8749	0.0121
NK	1	1
SC	1.44	1
PSNR	24.08	40.7195

Table 2 shows the measurement parameters employed between the test image Mandrill and the encrypted Image and between the original image and its decrypted image.

TABLE II. QUALITY MEASURMENT PARAMETERS FOR TESTIMAGE 2

Measurement Parameters	**Comparison between Original Image Lena and Encrypted Image**	**Comparison between Original Image Lena and Decrypted Image**
MSE	245.67	. 5.5150
AD	93.06	1.5023
MD	238	5
NAE	0.8584	0.0139
NK	1	1
SC	1.4266	1.0004
PSNR	24.2271	40.7154

V. Conclusion

This paper presents a new image encryption method based on a hybrid model of encryption using various encryption techniques. Experimental results show that our model yields high random cipher image measured by various quality measurement parameters such as MSE, AD, MD and PSNR thus making it difficult to recover the original image without the key.

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Energy Management with Disaster Intimation and Control using IoT

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***Abstract* - In the area of digitization and automation, the life of human being is getting simpler as almost everything is automated. Nowadays humans have made internet an integral part of their everyday life without which they are helpless. Internet of things (IoT) gives a platform which allows different devices to inter-connect, sense and control the things remotely across a network infrastructure without any limitation to the coverage area. In our proposed work, we stress on Wireless-Home-Automation-System (WHAS) using IoT, it is a system uses computers or smart phone to control basic home functions and features automatically through internet from anywhere around the world, an automated home is sometimes called a smart home. The proposed system is able to monitor the entire things connected to the internet and also to be maintaining the status of individual devices for further action. We have built the home automation with several devices and sensors, here sensor help to monitor the device status and intimate the authorized person to take particular action.**

Keywords-Home Automation System, IoT, data storage, Raspberry Pi 3B, Web monitoring, Security credential

I. INTRODUCTION

The internet on things is the most upcoming popular application used and adopted by worldwide. In this application the authorized user can access the data and acknowledge on the particular things from irrespective of place, the internet on things made a human life much easier way to handle the things or devices from anywhere with internet on smart phone or personal computer. The system should be able to encrypt the authorized credential and protect from the third party attacks, The internetworking of physical devices, vehicles, buildings and other items embedded with electronics, software, sensors, and network connectivity that enable these devices to collect and exchange data. Internet on things leads to better and comfort on energy management as it will be able to control the device status and take action as per desired outcome. The Energy will be inexorably linked to the internet on things. The many number of devices, industries, buildings, transport systems and smart cities are connected and controlled through the Internet.

1.1 Need for Automation

Enough progress in home automation technology occurred to make it worthwhile to “smarten” up our home. The purpose of being able to control your security system from afar and cut your energy costs. Ultimately, at some point, our various home appliances could be connected, allowing us to control them all from our phones or another type of device. For now, some appliances can be controlled by using a Wi-Fi Connection, but you need separate smart phone apps or devices to tell them what to do. We won’t even need to touch a button (for instance, you could simply walk into a room and your curtains would open, the temperature would turn up, and your favorite song would start playing). Ultimately, if it’s set up with compatible devices and connect with one software platform, one could have a controlled, “smart” environment. Some home security systems are getting pretty close, giving users the ability to control temperatures and see who knocks at their door when they’re away from home Tying Security cameras into home automation system allow to use an app or other sources to see when a visitor arrives, whether it's an actual delivery person or a thief posing as a delivery person. By using the home automation systems with a front door camera, one can see any visitors and respond to them audibly, making it appear as though we're home even when we are many miles away.

II. RELATED WORK

Work [1] proposes an Advanced Home Automation system using Open source Android, in this review paper many technologies for implementing Home automation systems were discussed and compared too. The Method used to implement and Limitations of the respective Home Automation System are discussed. "IoT based Interactive industrial Home wireless system, Energy Management System and embedded data acquisition system to display on webpage using GPRS,SMS and E-mail alert", In this paper the microcontroller ARM LPC2148 is used to implement the hardware and data acquisition. UART terminals UART0 interfaced with Zigbee module and UART1 with GSM module [2]. Several sensors are interfaced to the processor along with the LCD, for the data

read by the sensors all the time. The data is stored in the flash memory of the processor. Flash memory interfaced to the processor through SPI protocol. The measured values are transmitted to the control unit via Zigbee, displayed on the computer and sent to the internet via WAN, here the drawback is using Zigbee protocol for data acquisition and the implementation cost to build the network increases with the size of network. [3] A Home Automation system using Internet of things to control household appliances remotely. The microcontroller used in this work is Intel Galileo. Here all the devices connected to the internet are continuously monitored and the data is saved on the cloud. The webpage is built using the HTML language and cloud computing is practiced. [4] In this work proposes Enabling IoT services for Wifi-Zigbee gateway for Home automation. This system uses Cubietruck board interfaced with wifi module (gateway) and uses TCP/IP communication protocols to enable internet. Cubietruck transmits sensor data to wifi through communication protocols. The gateway provides methods to access the sensors for user interaction and bridges interconnection between different protocols.

This primary objective of this paper is to design a Home Automation system that employs the integration of multi-touch mobile devices, cloud networking, wireless communication, and power-line communication to provide the user with remote control of various lights and appliances within their home. This system uses a consolidation of a mobile phone application, handheld wireless remote, and PC based program to provide a means of user interface to the consumer [5].

III. System Analysis

3.1 Problem Definition

Energy Management is an increasingly critical focus area for utilities and energy service providers, as well as end customers. Energy consumption needs to be minimized without compromising on comfort and other ergonomic considerations. An efficient energy management system helps optimize energy consumption. An advanced energy management system can ensure monitoring of building conditions, equipment status, utility sub-metering. Such system can also focus on maintenance (remote operation and control of equipment).

3.2 Objectives

The main objective is to design and implement a system using IoT, to limit the unnecessary energy flow commercially as well as in industrial level. The main challenges are high cost of ownership, deploy communication system to manage, make use of pre-installed devices to run the system.

IV. Proposed System

We will be making use of Raspberry pi 3B interfaced with Pi camera module and PIR sensor for Motion Detection. Flame Sensor is also interfaced on the Raspberry PI for Detecting Disaster in households through fire. For controlling the electrical Appliances which run on AC, we make use of Relay boards. Here we are using two channel Relay Boards, converting the input working on 12 V DC to 240V AC. To provide Raspberry Pi with the internet we can connect our processor to LAN through Wi-Fi or enabling internet through LAN cable or through Dongle connected to one of the USB ports. It's necessary that the processor (Raspberry Pi) is always connected to the internet. Also connected to the GSM. The Emergencies are called via GSM interfaced to the Raspberry Pi.

4.1. System Design & Implementation

The following figure 1 shows the block diagram of the proposed system. The sensors are used here to monitor the status and we have connected many devices through the relays and will be controlled by Raspberry pi with GSM through which the authorized user command the instruction to the system and control the device status.

4.2. Proposed System Functions

The Proposed system can monitor the following sensors and components:

- Motion Detection
- Fire and Smoke Detection
- The proposed System can control following appliances:
- Lights on/off
- Fans on/off

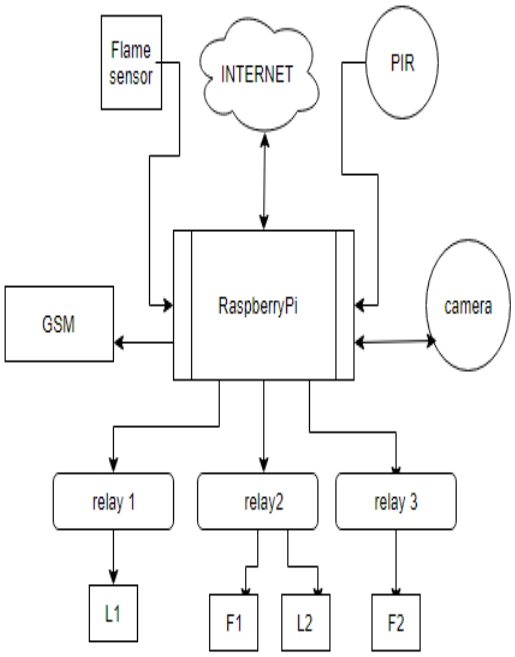

Figure 1. Proposed System Block Diagram

4.3. Software Design

The front end for the webpage is designed using HTML and CSS. Backend design is PHP at the server-side and Java Script at the client side.

4.4 System Implementation and Working

As the main aim of the project is to optimize the energy used by the electrical appliances in households, industries, buildings, or an entire city and can be accomplished by laying an inter connection between all the devices(controllers) used in various areas to the internet which ultimately results in Internet of Things(controllers).To find out who has s been in the house, A parent detector such as the motion detection is connected to raspberry pi, when any unauthorized intrusion occurs, video triggering starts via Raspberry Pi camera module. It records the video with date and time labels (filename).Therefore; this can also be a security to the household. User's privacy concerns a lot in this system, the webpage holds the control through the pre-installed camera at the area of operation. Camera captures the images, the moment it detects the motion automatically and sends the copy of the image to the drop box. Here the drop box acts as a database or a cloud which holds the images from the camera. A flame sensor is deployed on the raspberry pi, such that if any disaster happens in the house such as Kitchen fire or short-circuits fire, an immediate call is made to the emergencies.

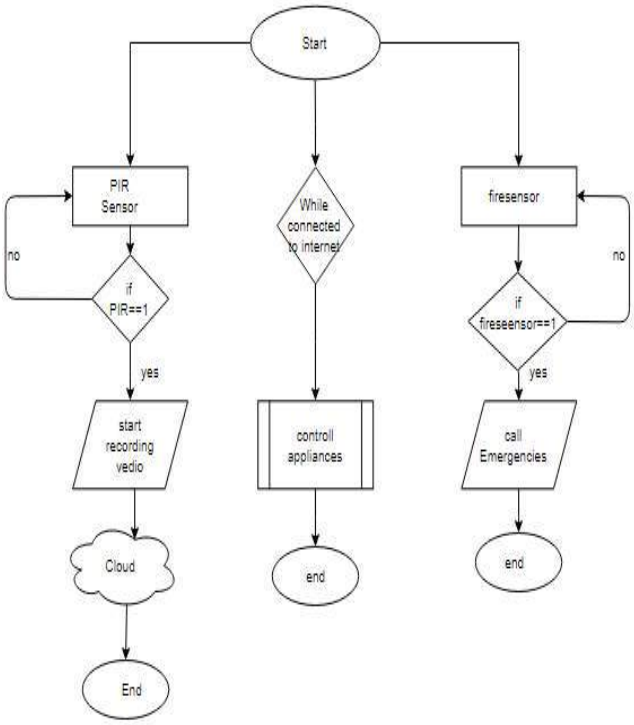

Figure 2. System flow graph

Step 1: Monitors for the intrusion, if any intrusion gets detected i.e., PIR senses change in the IR signature and turns ON the Pi camera installed on the RPi to start either recording or captures the images the moments soon after it detects the intrusion. Through GSM a notification at the end user can be sent in the form of a text message via GSM module. The captured image or video is uploaded on to the Drop box. This can be previewed by logging into the registered Drop box account. (Webpage or application)

With intrusion detection, the electrical appliances can be turned on automatically.

Step 2: Monitors for the disaster in the household, if fire explodes i.e., the module makes use of fire sensor and comparator for the change in the IR radiation from the flame. A Call will be made to emergencies, indicating there is an emergency situation and a buzzer interfaced on the raspberry pi acts as alarm, and is activated on for the fire explosion.

Step 3: While connected to the internet, the electrical appliances can be controlled remotely.

The second stage is actually the controlling stage in which all the electrical appliances can be accessed through the internet, Controlling the appliances in the household from remote place can be done just by knowing the IP address of the network to which the raspberry pi is connected to, that can be either through an android application or through a web address containing a layout of all the appliances. In order to gain the access over the layout the user has to login with a unique password. Here The IP address of the Raspberry Pi can be held fixed by port forwarding.

V. Results & Discussion

The proposed system is shown with figure 3, the number of sensors and devices like: speaker, motion detector, light etc.

Interface of PIR sensor and camera module on RaspberryPi is shown in Fig.13. The PIR sensor which is connected will detect the motion if any and will send the input to RaspberryPi. As soon as the motion is detected the camera gets active and will capture the image and video of the intrusion. This will be stored in the Raspberry Pi and also will be sent to Drop box.

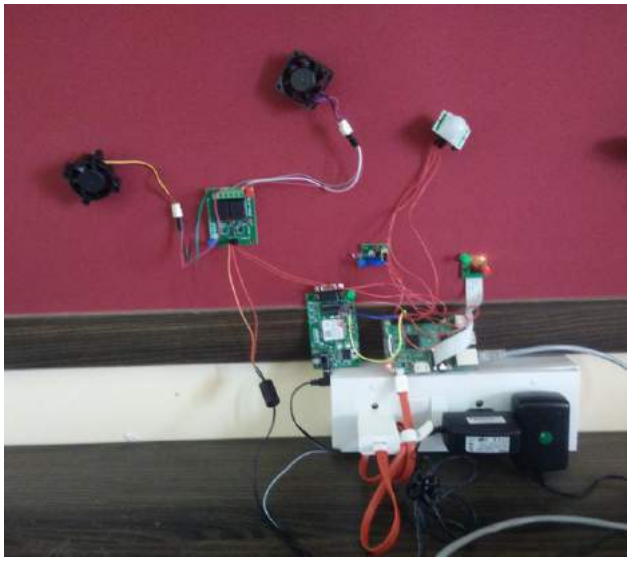

Figure 3. Entire setup of the sensors and the processor.

The code written in python script is simulated on the terminal before burning the code on the processor, and when the motion is detected the following figure 4 shows the

terminal output and the same captured video or the image is uploaded to the respective cloud the figure 5. Illustrates the Drop box upload from the pi, with date and time mentioned.

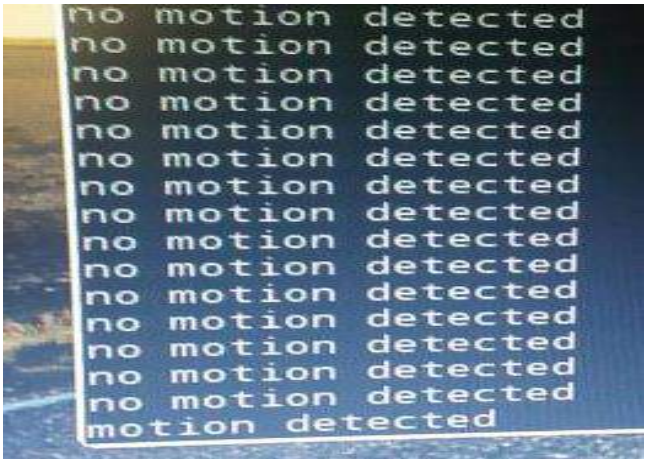

Figure 4. Motion Detection

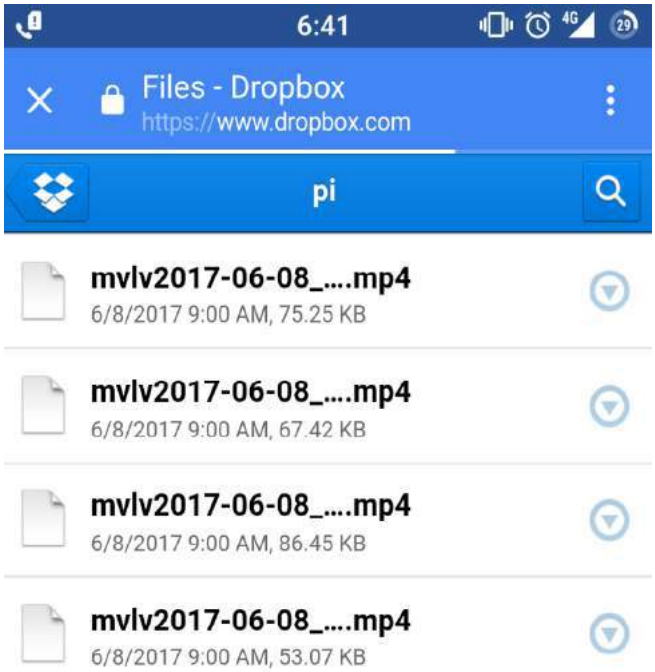

Figure 5. Drop box upload from Pi.

Similarly when the Fire explosion takes place the flame sensor reads the value high and sends the same to the processor, as the input to the processor from the sensor is high, a call is being made to the emergencies. The same is shown in Figure 6. The connections are shown in Figure 6(a) and when fire is detected the sensor reading high is shown in Figure 6(b). Interface of buzzer on RaspberryPi through which it is alarmed and Figure 6(c) shows the terminal output of fire detection.

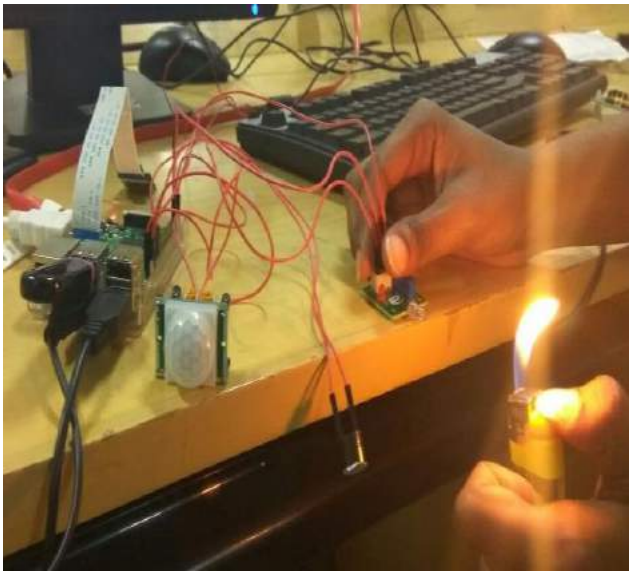

Figure 6(a). Flame sensor detecting fire and alarmed thru buzzer

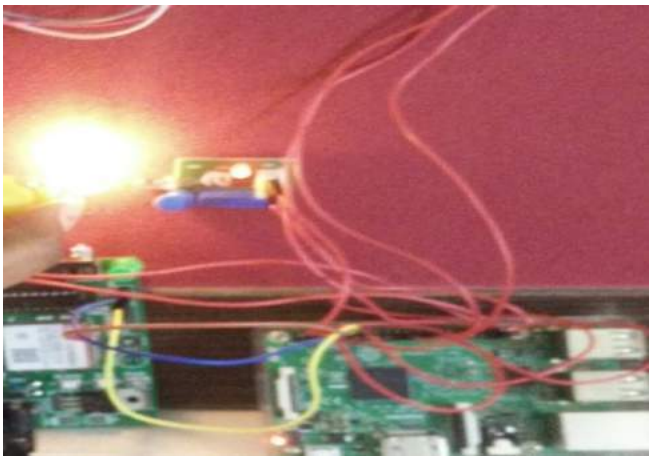

Figure 6(b). Sensor reading High When Fire Explodes.

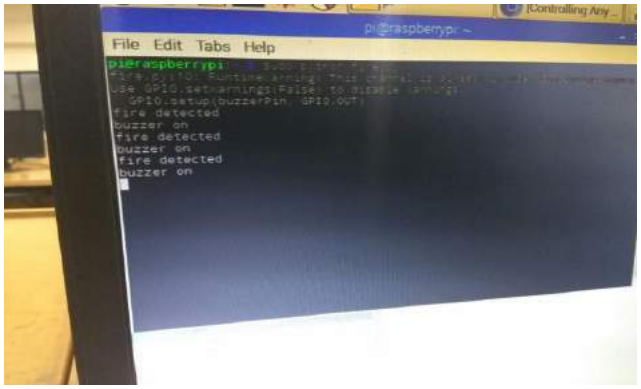

Figure 6(c).Terminal output after flame detection

When fire is detected by the sensor module, then it will write digital high output on the flame sensor. The out is read by

RaspberryPi on pin18. Depending on the status of the pin, Buzzer is activated and GSM module will place the call.

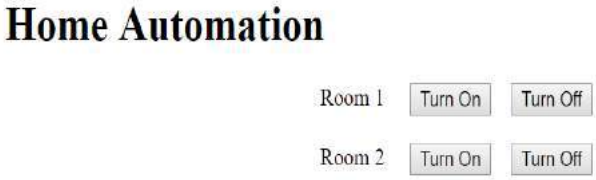

Figure 7. Webpage view for on and off.

The above figure shows the layout of the switch buttons for switching on/off electrical appliances for different rooms in a household. The webpage is created using HTML and PHP languages. The webpage contains login and password too. This varies according to the ip address of the client.

VI. Conclusion

The home automation using Internet of Things has been experimentally proven to work satisfactorily by connecting simple appliances to it and the appliances were successfully controlled remotely through internet. The designed system not only monitors the sensor data, like fire, motion sensors, but also actuates a process according to the requirement, for example switching on the light when it gets dark. It also stores the sensor parameters in the cloud (Drop Box) in a timely manner. This will help the user to analyze the condition of various parameters in the home anytime anywhere. Using this system as framework, the system can be expanded to include various other options which could include home security feature like capturing the photo of a person moving around the house and storing it onto the cloud. This will reduce the data storage than using the CCTV camera which will record all the time and stores it. The system can be expanded for energy monitoring, or weather stations. This kind of a system with respective changes can be implemented in the hospitals for disable people or in industries where human invasion is impossible or dangerous, and it can also be implemented for environmental monitoring.

Automation of Turning on the cylinders, depending upon type of fire detected fixed in buildings can be made. Safety measures can be scientifically automated and should be easily operatable using advanced sensors and processors.

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Kinetics and Solvent Effect on Hydrolysis of Ethyl Cinnamate in Water-Methanol Mixture

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***Abstract*— The solvent effect of aquo-dipolar protic solvent system was highlighted by studying the kinetics of base catalyzed solvolysis of ethyl cinnanmate in water-methanol media of various compositions having 20 to 70% (v/v)of ethanol at different five temp ranging from 20 to 40^{0}C. Fast decrease of specific rate constant with gradual addition of organic co solvent in the reaction media and also with increasing temperature of the reaction has been explained in light of solvation in initial and transition state to different extent. The change in Iso-composition Activation energy (E_C) and Iso-dielectic Activation energy (E_D) also explained the solvation and desolvation of initial and transition states to different extent The decrease in number of water molecule (1.59 to 1.42) associated with the activated complex is found to be decrease in water-MEOH system and this tells about the fact that in presence of MEOH the mechanistic path of reaction is change from bio-molecular to uni-molecular. Increase in numerical value of free energy of activation (ΔG^*) simultaneous decrease in entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*), of reaction media reveals that ethanol acts as entropy inhibitor and Enthalpy stimulator.**

Keywords - ***Solvent effect, ethyl cinnamate, Hydrolysis water-methanol mixture. Specific rate constant, Iso-composition and Iso-dielectric Activation energy, Activated complex.***

I. INTRODUCTION

The effect of solvent on the rate and mechanism of alkali catalyzed hydrolysis of ester have received continued attention, but the explanation put forward is not satisfactory [1-3]. So, in order to explore the above idea, it was thought essential and useful to investigate about the fact that how ethyl cinnamate is useful as flavor and fragrance agent in cigarettes and cut tobacco. This compound is also used as food additive for human beings.

II. EXPERIMENTAL

Kinetic of alkali catalyzed solvolysis of ethyl cinnamate was studied by adding different concentrations of the protic organic co solvent(methanol) from 30 to 70%(v/v) in reaction media at five different temperature i. e. 20^0, 25^0, 30^0, 35^0 &40^0 using volumetric method. All chemicals used were either of BDH or Merck grades. The strength of the solution was kept 0.1M with respect to NaOH and 0.05 M with respect to ester. The reaction rates were determined by titrating the sample at different time interval using phenolphthalein indicator. The specific rate constant value was calculated using second order reaction and tabulated in Table-I. Variation of specific rate constant with different mole% and different temperature are inserted in Table-2.

The value of slopes of Arrhenius plot of logk verses 1/T (Table-3) (Iso-composition activation energy (E_c) and plots of logk verse D (Iso-dielectric activation energy) were evaluated and inserted in Table-4&5 respectively. From the plots of Logk verses Log [H_2O] Table-6, the value of slopes were evaluated and tabulated in Table-7. Thermodynamic Activation Parameter were also calculated and inserted in Table-8

III. RESULT AND DISCUSSION

3.1 Solvent Effect on Specific Rate

In order to highlight the effect of the solvent on specific rate constant values(Tab-I) of the reaction, the logk values were plotted against the mole% of organic co-solvent(their values from Table-2 as shown in fig-1) and were found to show decreasing trend. The plots show that with increase in the temperature of the reaction, the degree of depletion in the rate constant of the reaction becomes slower. However, the possible rate depleting factors in the rate can be enlisted as follows:

1. Decrease in bulk dielectric constant value of medium,
2. Decrease in the polarity of the reaction media by adding less polar methanol to it.

The above noted two depleting factors are quite in operation and are with good agreement with theory of Hughes and Ingold [4] that rate ought to decreases with decreasing dielectric constant of the reaction media. Such decrease in rate constant with increasing proportion of organic co-solvent like methanol have also reported by Elsemongy [5], and recently by Singh A K[6].

TABLE I. SPECIFIC RATE CONSTANT K X103(DM)3/MOLE/MINT]VALUES OF ALKALI CATALYZED HYDROLYSIS OF ETHYL-CINAMATE IN WATER-METHANOL

Temp in ^{O}C	% of Methanol				
	30%	40%	50%	60%	70%
20°C	8.31	6.60	5.43	4.46	3.75
25°C	2.56	9.74	7.85	6.59	5.37
30°C	18.15	13.96	11.09	9.12	7.58
35°C	26.24	19.90	15.48	12.88	10.47
40^{0}C	27.15	28.18	21.57	17.78	14.45

TABLE II. VARIATION OF 3 + LOGK VALUE AGAINST MOLE %,(WATER-METHANOL) SYSTEM

Temp in ^{O}C		3 + Logk				
	Mole%	20°C	25°C	30°C	35°C	40^{0}C
30%	16.03	0.920	1.099	1.259	1.419	1.570
40%	22.90	0.820	0.989	1.145	1.299	1.450
50%	30.82	0.735	0.895	1.045	1.190	1.330
60%	40.06	0.650	0.819	0.960	1.110	1.250
70%	50.97	0.565	0.730	0.880	1.020	1.160

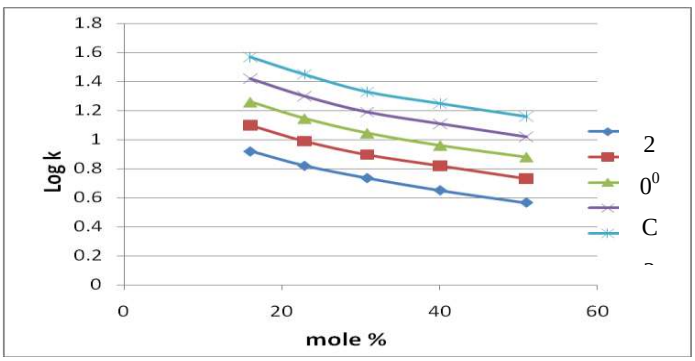

Figure 1. Variation of 3+Log k with mole% (water-methanol system)

3.2 Solvent effect on Iso-composition Activation Energy of the reaction

From Tab- 4, (Fig-2) it is found that the values of Iso-composition Activation Energy goes on increasing [52.16 to 57.37kj/mole] with increasing concentration of MEOH from 30% to 70%(v/v) in reaction media. The increasing trend in the E_{exp} values can be explained by any of the following three situations.

1. Transition state is desolvated less than Initial state
2. Transition state is solvated more than the initial state
3. Transition state is solvated and initial state desolveted.

The transition state being large cat ion (ester + H+) is available more for solvation by methanol molecule than the initial state, so third factor seem to operative in my case and is also supported by decrease in entropy of activation (□S*) . This conclusion is also supported recently by Singh R. T. et al.[7]

TABLE III. 3 + LOGK VALUE AGAINST 10^3/T, WATER- METHANOL SYSTEM

Temp in ^{O}C		3 + Logk				
	10^3/T	30%	40%	50%	60%	70%
20°C	3.412	0.920	0.820	0.735	0.650	0.575
25°C	3.355	1.099	0.989	0.895	0.819	0.730
30°C	3.300	1.259	1.145	1.045	0.960	0.880
35°C	3.247	1.419	1.299	1.190	1.110	1.020
40^{0}C	3.195	1.570	1.450	1.330	1.250	1.160

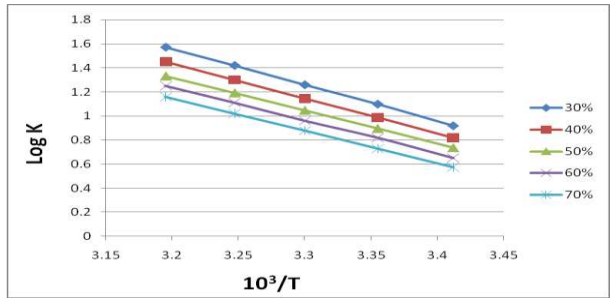

Figure 2. Variation of 3+Logk against 10^3/T (Water-methanol) system

TABLE IV. VALUES OF ISO-COMPOSITION ACTIVATION ENERGY (WATER-MEOH MEDIA)

% of MEOH	30%	40%	50%	60%	70%
E_{exp} in KJ/mole	52.16	52.74	54.30	54.30	57.37

3.3 Solvent effect and Iso- Dielectric Activation Energy

From the slope of Arrhenius plot of $logk_D$ values against 1/T, the value of iso-dielectric activation energy has been evaluated and recorded in Tab-5. From the table-5 and Fig-3, it is inferred that E_D value goes on increasing from 55.45 to65.09 kj/mole with increasing D values. This trend of variation is similar as E_c values (62.31to64.88 KJ/mole) (Tab-5) with gradual addition of more solvent in reaction media. This interpretation was supported by past view of Wolford [8] recently supported by Singh R T. et al.[9]

TABLE V. VALUES OF ISO-DIELECTRIC ACTIVATION ENERGY (WATER-METHANOL)

Dielectric constant(D)	D=45	D=50	D=55	D=60	D=65
E_{exp} in KJ/mole	55.45	57.95	62.19	62.76	65.09

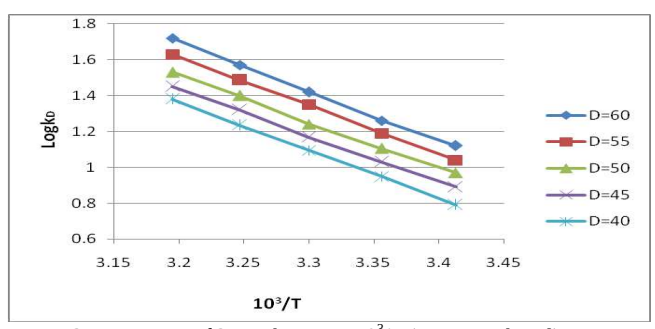

Figure 3. Variation of 3+Logk against 10^3/T (Water-methanol) system

3.4. Effect of concentration of water molecules [H_2O], associated with the Activated complex on mechanistic path of the reaction

The effect of water concentration [H_2O] of the water-ethanol mixture, on rate and mechanism of alkali catalysed hydrolysis of ethyl cinnamate has been studies. For this, the number of water molecule associated with activated complex was determined by plotting Log k against Log[H_2O], According to Robertson[10] relation

$$\log k = \log k_0 + n\log[H_2O]$$

Here n is the solvation number and decide the criteria about the mechanism of reaction.

From noted value of slope mention in Table-7, it may be seen that with rise of temperature from 20 to 70^{0}C, the value of slope (number of water molecule associated with activated complex) goes on increasing from (2.08 to 2.56). This observation may be attributed to the fact that with addition of ETOH in reaction media, the equilibrium of water component reaction media shifted from its dense form to its bulky form with rise of temperature.

$$[H_2O]_d \square [H_2O]_b$$

Finally, it is inferred that with rise of temperature, the number of water molecule associated with activated complex increases as the proportion of bulky form of water molecule increase with increase in MEOH content in the water-ethanol mixture and it explain that when MEOH is added to water, the mechanistic path of reaction is changed from biomolecular to unimolecular in similar way as observed by parker and Tomilinson[11] and recently by Singh A K [12]

TABLE VI. Variation of 3+ Log k with log [H2O] (water – methanol) at different temperature

% of Acetone	% of H_2O	Log [H_2O]	3 + Log k				
			20^{0}C	25^{0}c	30^{0}c	35^{0}c	40^{0}c
30%	70%	1.5690	0.890	1.075	1.210	1.70	1.570
40%	60%	1.5229	0.820	0.989	1.145	1.290	1.500
50%	50%	1.4437	0.735	0.895	1.045	1.190	1.390
60%	40%	1.3468	0.650	0.819	0.965	1.090	1.280
70%	30%	1.2218	0.565	0.730	0.880	0. 980	1.160

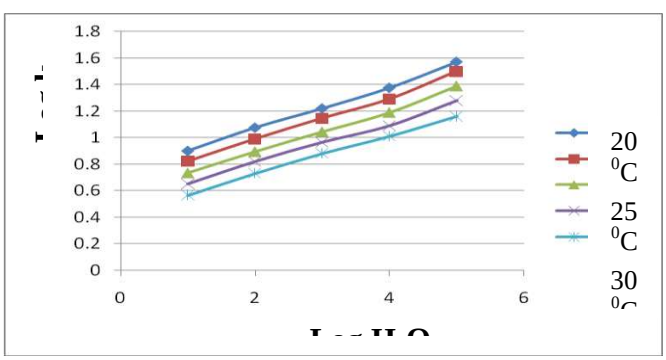

Figure 4. Variation of 3+Logk against 10^3/T (Water-methanol) system

TABLE VII. Calculated values of slopes (Plot of log k verses log [H_2O]) of Water-methanol media

Temp^{0}C	20^{0}c	25^{0}c	30^{0}c	35^{0}c	40^{0}c
Slope	2.08	2.16	2.21	2.29	2.56

TABLE VIII. Consolidated values of Thermodynamics Activation Parameters($\Delta H^*$and ΔG^* in KJ/Mole, ΔS^*in J/K/Mole)of the reaction in Water- methanol Media

% of MEOH	Mole %	ΔH^* in Kj/Mole	20^{0}C		25^{0}C		30^{0}C		35^{0}C		40^{0}C	
			ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
30 %	16.03	53.31	93.64	137.64	94.27	137.44	94.98	137.52	95.60	137.30	96.31	137.38
40 %	22.90	52.95	94.20	140.78	94.91	138.42	95.65	140.89	96.31	140.77	97.03	140.83
50 %	30.82	52.87	94.68	142.6	95.44	140.30	96.23	143.10	96.96	143.14	97.75	143.38
60 %	40.06	51.28	95.16	149.76	95.88	147.24	96.72	149.96	97.43	149.83	98.23	150.00
70 %	50.97	50.51	95.64	154.02	96.39	151.44	97.19	154.05	97.96	152.56	98.77	154.18

IV. Conclusion

In hydrolysis of Ethyl cinnamate, the decreasing trend of specific rate constant at all temp with increasing mole% of co-solvent which show that the decrease is either due to bulk dielectric constant value of medium or decrease in the polarity of the reaction media by adding less polar methanol to it. The values of Iso-composition Activation Energy goes on increasing [52.16 to 57.37kj/mole] with increasing concentration of MEOH from 30% to 70%(v/v) in reaction media indicate Transition state is solvated and initial state desolveted.Increase in the value of and ΔG^* with simultaneous increase in ΔH^* &ΔS^* for the hydrolysis ethyl cinanimate in water- Methanol is enthalpy dominating and Enthalpy control. The linear plots obtained by plotting logk as function of D represent the different electrostatic interaction for the ion-dipole as well as dipole - dipole reaction. Solvating power of MEOH change the mechanism of the reaction from bio-molecular to unimolecular due to increase in number of water molecule associated with activated complex (2.08to 2.56).

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Heterogeneous Spectrum Sensing in Cognitive Radio Network using Traditional Energy Detection and Matched Filter

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***Abstract*— The accurate spectrum sensing is a predominant aspect of any competent CR system. Efficient spectrum sensing enables a CR terminal to detect the spectrum holes (underutilized spectral bands) by providing high spectral resolution, thereby accrediting opportunistic transmission in the licensed band to the CR. In order to facilitate a good spectrum management and its efficient use a hybrid method for the detection of the spectrum with the purpose of detecting the presence of bands of unoccupied frequencies is proposed. The method used are traditional energy detection and matched filter with changing number of secondary users using each technique and finally a centralized cooperative spectrum sensing network which employs hard combination at the fusion centre.**

Keywords- ***cognitive radio; spectrum sensing; energy detection, ROC; Matched Filter***

I. INTRODUCTION

Given the limitations of the natural frequency spectrum, it becomes obvious that the current static frequency allocation schemes cannot accommodate the requirements of an increasing number of higher data rate devices. As a result, innovative techniques that can offer new ways of exploiting the available spectrum are needed. Cognitive radio arises to be a tempting solution to the spectral congestion problem by introducing opportunistic usage of the frequency bands that are not heavily occupied by licensed users. In effect, this approach proposes to a new category of users so-called secondary users (SUs) to access the frequency resources allocated to primary users (PUs) when the latter do not use them [1]. Primary users can be defined as the users who have higher priority or legacy rights on the usage of a specific part of the spectrum. On the other hand, secondary users, which have lower priority, exploit this spectrum in such a way that they do not cause interference to primary users. Therefore, secondary users need to have cognitive radio capabilities, such as sensing the spectrum reliably to check whether it is being used by a primary user and to change the radio parameters to exploit the unused part of the spectrum. Thus, the spectral efficiency is increased by allowing the transmission by the SUs on frequency bands detected free .

Being the focus of this paper, spectrum sensing by far is the most important component for the establishment of cognitive radio. Spectrum sensing is the task of obtaining awareness about the spectrum usage and existence of primary users in a geographical area. The detection of the spectrum is hence a crucial task for the success of the opportunistic access. It is a cardinal feature of cognitive radio to avoid harmful interference with authorized users and recognize the spectrum available to improve the use of the spectrum.

There are several spectrum detection techniques. In the scope of this paper we have evaluated the results of spectrum detection using traditional energy detection and then compared the result with proposed hybrid sensing wherein a certain percentage of the nodes where using traditional energy detection and the remaining were designed to use matched filter detection for different number of secondary users.

Finally concept of cooperative spectrum sensing for cognitive radio networks is implemented to combat difficulties such as multipath fading, shadowing and receiver uncertainty issues. Here the information collected by each node is reported in the form of single or multi bit decisions called hard combination to the fusion centre which uses a majority rule to form final decision on the presence of primary user PU.

II. MATHEMATICAL MODELING FOR SPECTRUM SENSING

Spectrum sensing [2] is based on the signal detection theory and a sensing device can be viewed as a binary classifier making a decision out of a two hypothesis test where the hypothesis H0 and H1 represent the absence and presence of a PU respectively.

$$y(k) = \begin{cases} n(k) & : \ H0 \\ n(k) + p(k) & : \ H1 \end{cases} \tag{1}$$

Here y (k) represents the detected signal, n (k) represents noise and p (k) refers to the PU signal. Four possibilities exist for the detection:

Declaring H0 when H0 is true (H0|H0): Correct Detection.

Declaring H1 when H1 is true (H1|H1): Correct Rejection.

Declaration H0 when H1 is true (H0|H1): False Alarm.

Declaring H1 when H0 is true (H1|H0): Missed Detection.

Thus, correct detections are the true positives, correct rejections are the true negatives, false alarms are the false

positives and missed detections are the false negatives for the spectrum sensing test [3].

III. SPECTRUM SENSING METHODS FOR COGNITIVE RADIO

A number of different methods are proposed for identifying the presence of signal transmissions. In this section, some of the most common spectrum sensing techniques available in the cognitive radio literature is explained.

A. *Energy Detector Based Sensing*

Energy detector based approach, also known as radiometry or period gram, is the most common way of spectrum sensing because of its low computational and implementation complexities. In addition, it is more generic (as compared to methods given in this section) as receivers do not need any knowledge on the primary users' signal. . The traditional Energy Detector [4] simply measures the energy of the received signal over a fixed interval termed as sensing interval. The average energy calculated over the sensing interval becomes the test statistic. The test statistic is then compared with a pre defined threshold. If the value of the test statistic is greater than the value of the threshold, the frequency being sensed is declared to be occupied otherwise it is declared as free to be used by the SU.

The design and performance parameters of traditional energy detector are the characteristics that are input to its design process. An energy detector is designed for a desired false alarm probability. The target probability of false alarm decides the threshold employed in the decision logic. Thus for any energy detector the false alarm probability and decision threshold are predefined. The performance parameters include the probability of detection at the given desired probability of false alarm.

- Design parameters

  An energy detector is designed for a predefined value of false alarm probability (Pf) which also sets the decision threshold .For a target probability of false alarm Pf, the threshold and probability of detection and be expressed in terms of the inverse Q function of the target false alarm probability given by equation

$$\boldsymbol{\lambda} = \sigma^2\left[\sqrt{\frac{2}{N}}Q^{-1}(\,\mathrm{Pf}) + 1\right] \tag{2}$$

Here Pd, Pf, λ represent the probability of false alarm, probability of detection and decision threshold for traditional energy detection respectively. Q represents the Q tail function, N and γ represents the length of sensing interval and SNR observed at the node.

- Performance Parameters

For any energy detector designed for a particular target frequency and employing a given threshold, probability of detection is given in terms of the Q function (tail probability function of the normal distribution)

$$Pd = Q\left\{\frac{\left[\left(\frac{\lambda}{\sigma^2}\right)-\gamma-1\right]\sqrt{\frac{N}{2}}}{\gamma+1}\right\} \tag{3}$$

Here Pd, Pf, λ represent the probability of false alarm, probability of detection and decision threshold for traditional energy detection respectively. Q represents the Q tail function, N and γ represent the length of sensing interval and SNR observed at the node.

Some of the challenges with energy detector based sensing include selection of the threshold for detecting primary users, inability to differentiate interference from primary users and noise, and poor performance under low signal-to-noise ratio (SNR) values. Moreover, energy detectors do not work efficiently for detecting spread spectrum signals.

B. *Matched Filter Detection*

Matched Filter Spectrum Detection: If SUs know the information about a PU signal [5] a priori, in this case, the optimal detection method is the matched filter since it maximizes the SNR of the received signal. Detection MF needs just a little time in order to obtain a good performance unlike other methods, such as the low probability of false alarm and missed detection, since the MF has less need for the samples received. As disadvantages, MF has an implementation complexity and high power consumption, because of the need of the detector receivers for all types of signals and the algorithms of corresponding receiver to be executed. The process screening requires a perfect knowledge of the PU signal and its frequency of operation, for example, the modulation type and order, the bandwidth, the pulse shape, packet format etc [6]. Whenever the information used by the matched filter is false the efficiency of the detection will be degraded, which leads to distortion of the CR concept and from the PU's perspective, may cause low QoS for the licensed users.

The matched filter is a system of linear filter used in the framework of the digital signal processing. It is used to optimize the SNR in presence of the additive noise stochastic. It provides the coherent detection. A signal received from primary user is transmitted through AWGN (Additive White Gaussian Noise) channel and the transmitted signal is applied to matched filter. Matched filter correlates the signal with time modified version and comparison between the predetermined threshold and the final output of matched filter will determine the presence of the primary user.

If y (k) is sequence of received samples at instant k ∈ {1, 2. . . N} at the signal detector, the decision rule can be stated as

$$\text{Decide for } \begin{cases} H0, & if\ \hat{S} < \gamma \\ H1, & if\ \hat{S} > \gamma \end{cases} \tag{4}$$

Where $\hat{S} = \sum_{k=1}^{N} y(k)x(k)^*$ is the decision criterion, γ is the threshold to be compared and $x(k)^*$ is the transpose conjugate of the input sequence [7][8].

$\hat{S}$ is Gaussian

$$\hat{S} = \begin{cases} \mathrm{N}(0, \sigma_n^2 \mathcal{E}), & H_0 \\ \mathrm{N}(\mathcal{E}, \sigma_n^2 \mathcal{E}), & H_1 \end{cases} \quad (5)$$

Where σ_n^2 is the variance of the noise and $\mathcal{E}$ is considered as the Energy of the signal [9] given by

$$\varepsilon = \sum_{k=1}^{N} x(k)^2 \quad (6)$$

Based on this, the probabilities of false alarm Pf and detection Pd are:

$$P_f = Q\left(\frac{\hat{S}}{\sqrt{\mathcal{E}\sigma_n^2}}\right) \quad (7)$$

and

$$P_d = Q\left(\frac{\hat{S}-\mathcal{E}}{\sqrt{\mathcal{E}\sigma_n^2}}\right) \quad (8)$$

IV. Hard Combination For Coperative Sensing

In this scheme, each cognitive radio (CR) user makes a decision on the state (presence or absence) of the PU and sends it in one bit form to the fusion center (FC). The main advantage of this method [10] is the easiness the fact that it needs limited bandwidth. Three rules for Hard Combination are described in the literature, these are AND Rule, OR rule and Majority rule. It was found that the Majority rule gave the best results and has been discussed below

K out of N or MAJORITY rule: Decides on the signal presence if at least K of the N users detected a signal with 1≤ K≤ N.

The K out of N rule is also known as Half Voting rule when K is greater than or equal to N/2 i.e. a PU is declared to be present only if half or more than half of the total CR users detect it. The K- out of- N rule boils down to the AND rule for K=N and to the OR rule for K=N. Thus, the K out of N rule [11][12] is the generalized form with AND and OR rules representing the two extremes.

V. Proposed Model For Heterogenous Co-Operative Sensing

As traditional energy detector fails in low SNR scenarios [13]. The improved detection algorithm efficiently manages to overcome these drawbacks by replacing some of the traditional energy detection nodes with matched filter detection. Hence instead of all the nodes carrying out spectrum sensing using energy detection a certain percentage detect the PU using matched filter technique [14]. To keep the overhead less all the nodes are not made to use matched filter and also matched filter requires coherent reception, which is generally hard to achieve in practice. So as to make a foolproof sensing process a balance is made between the adopted methodologies. Fig 1 describes the proposed block diagram

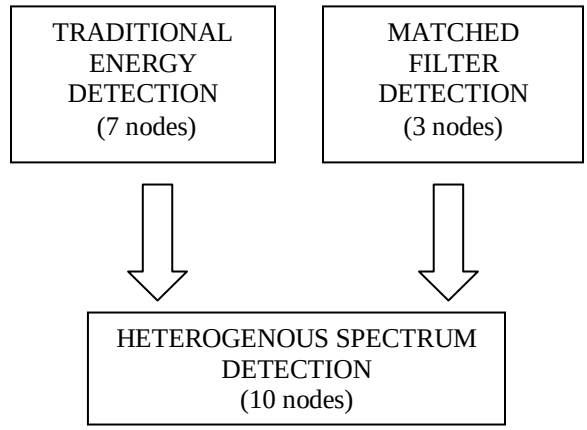

Figure 1. Proposed block diagram

VI. Simulation

As mentioned above, the matched filter detector performance is based on two parameters P_d andP_f. Performance is shown by plotting curve between the two called the Receiver Operating Characteristic (ROC) curve [15]. The simulation was focused on AWGN Channel. Each point of the curve corresponds to a value of the set (PD, PFA) for a given threshold. When threshold increases, P_d and P_f decrease and, when threshold decreases, P_d and P_f increase [16].

We consider a heterogeneous cooperative spectrum sensing for a centralized network consisting of a cognitive base station (fusion centre) and a number of nodes collaborating in a non fading (AWGN) environment [17] with perfect reporting and sensing channels. The network assumed employs the optimized energy detection described in section II, at every node, for local sensing and adopts hard combination for information fusion at the fusion centre. The simulations are done in MATLAB version R2013a for SNR= -14 db, the number of received signal samples L=100 [18] and for three sets of SU nodes such that the ratio of number of nodes operating on traditional ED to the number of nodes operating on MF is always 2.33 for optimal results.

In the first run 7 nodes are made to run on traditional energy detection and 3 nodes on matched filter. The obtained results are compared with 10 nodes running on traditional energy detection and the obtained ROC is plotted in Fig 2.

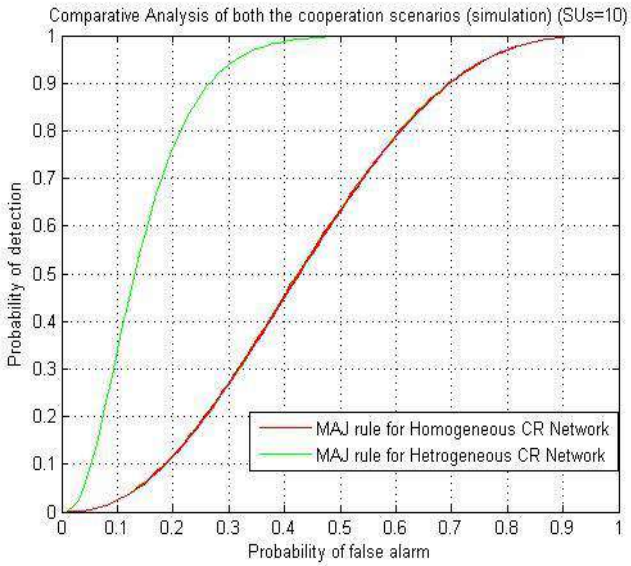

Figure 2. ROC curve for 7 traditional ED and 3 MF v/s 10 traditional ED

In the next run, 14 nodes are made to run on traditional energy detection and 6 nodes on matched filter. The obtained results are compared with 20 nodes running on traditional energy detection and the obtained ROC is plotted in Fig 3.

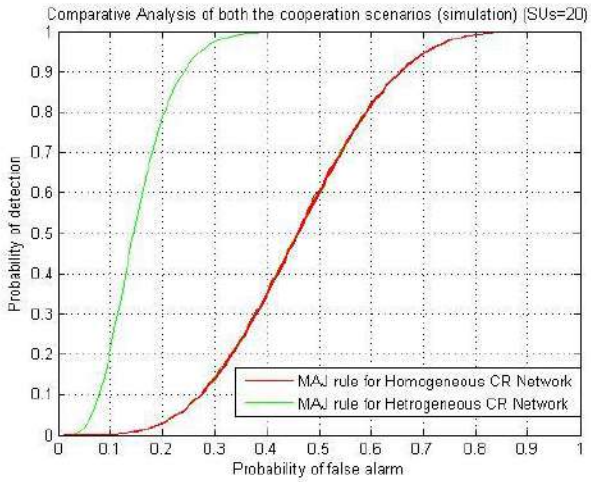

Figure 3. ROC curve for 14 traditional ED and 6 MF v/s 20 traditional ED

In the next run 35 nodes are made to run on traditional energy detection and 15 nodes on matched filter. The obtained results are compared with 50 nodes running on traditional energy detection and the obtained ROC is plotted in Fig 4.

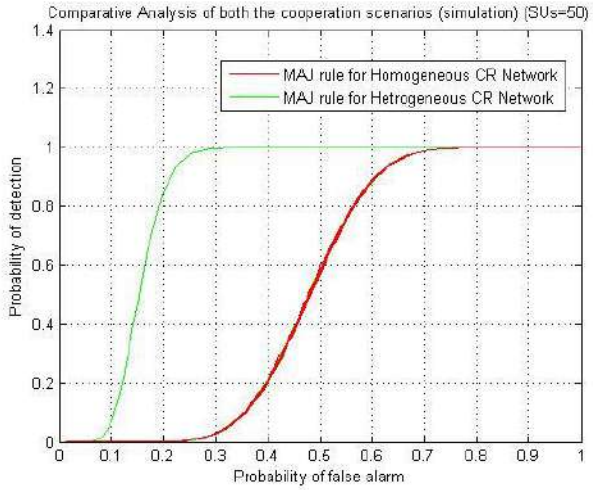

Figure 4. ROC curve for 35 traditional ED and 15 MF v/s 50 traditional ED

VII. Conclusion

In this paper, the technique for detection of the spectrum using a heterogeneous model employing the use of energy detection and matched filter is presented. The result obtained through the curves, shows that this method of detection maximizes the SNR of the received and probability of detection compared to the other homogenous methods.

In future traditional energy detection can be replaced by enhanced energy detector and other spectrum detection techniques can be explored.

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Studies of Solvent Effect of Aquo-Methanol Solvent System on Kinetics and Activation Parameters of Base Catalised Hydrolysis of Ethyl Cinnamate

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***Abstract*— The rate of alkaline hydrolysis of ethyl cinamate was measured over the temperature range of 20° C to 40° C in water-methanol mixture at different composition 30 to 70% (v/v).The specific rate constant was calculated using second order reaction. The influence of solvent variation on reaction rate was examined in term of changes in the Activation parameter. Depletion of ΔH^* and ΔS^* value with simultaneous increase in ΔG^* of the reaction in media, reveals that the reaction is Enthalpy domination and Entropy controlled. The Values of Iso-kinetic which is less than 300, clearly indicates that there is no appreciable interaction between solvent and solute present in the reaction media, i.e. reaction is not ion-dipole but ion-molecule type.**

Keywords- ***Activation Parameter, Solvent effect, solvent-solute interaction, Iso-kinetic temperature, specific salvation***

I. INTRODUCTION

Though the solvent effect on the rate and mechanism of the various type of reaction has been reported [1] [2] [3] but very little attention has been paid towards the study of the solvent effect on the thermodynamic activation parameter and solvent-solute interaction, particularly solvolysis of Ethyl Cinamate which is important for medicinal use as well as flavoring agent in cut tobacco. It has been proposed to make a kinetic study of the solvent effect on the base catalyzed hydrolysis Ethyl Cennamate in water-methanol media of various compositions.

II. EXPERIMENTAL

The kinetics of base catalyzed hydrolysis of ethyl acetate has been carried out volumetric in water-methanol and water-ethanol having different concentration of solvent (methanol) varying from 30 to 70% (v/v) at five different temperatures ranging from 20° C to 40° C at regular interval of 5° C. The specific rate constant calculated using second order reaction was found decrease with increase of methanol and ethanol content, tabulated in Table-I the evaluated thermodynamic activation parameter has been enlisted in Table-II.

III. RESULT AND DISCUSSION

A. *Solvent Effect on Specific Rate*

In order to highlight the effect of the solvent on specific rate constant values of the reaction, the specific rate constant were calculated with help of second order reaction and calculated values is inserted in Table-I . From Tab-1 it is observed that the values of specific rate constant is decrease with increase of temperature which is quite in agreement with theory of Hughes and Ingold[4] and Singh A K[5]

TABLE I. HYDROLYSIS OF ETHYL-CINNAMATE SPECIFIC RATE CONSTANT [K X10^3(DM)^3/MOLE/MINT]VALUES OF ALKALI CATALYZED IN WATER-METHANOL MEDIA

30%	40%	50%	60%	70%
15.66	11.22	10.00	8.12	6.45
20.89	16.59	13.48	10.59	8.49
27.54	21.87	16.98	13.64	10.83
38.01	30.19	23.17	18.62	14.62
45.70	36.30	27.86	22.38	17.74

B. *Solvent effect on Thermodynamic Activation Parameters of Reaction*

For better study of solvent effect on thermodynamic activation parameters, such as Enthalpy of activation (ΔH^*), Free energy of activation (ΔG^*), and Entropy of activation (ΔS^*) were taken into account as they have great significance. These parameters are calculated using Wynne-jones[6] and Eyring equation have been recorded in Table-II

In order to highlight the effect of solvent on these activation parameters, the value of these parameters were

plotted against mole% of methanol which is shown in figure 1, 2 &3.

From fig-2 and the value s of ΔG* recorded in Tab-II, obviously indicate that the variation in

ΔG* is small and it increases from 94.98to 97.19kj/mole at 30^0cwith change of proportion of methanol from 30% to 70% (v/v) The small but considerable increase in ΔG* and non linear variation in ΔH^* & ΔS* curves with the increasing mole% as shown in figure-1 and fig-3 are indication of specific salvation taking place in process of activation as already proposed by Saville &Hudson[7.] ,Tomilla et al.[8], Esemongy[9] and Cleve[10] have also observe the similar increase in ΔG* values. Increase in ΔG* with simultaneous decrease in

ΔH^* & ΔS* values is only possible when extent (degree) of depletion in ΔS* value is greater than ΔH* values and from this, it may be inferred that alkali catalysed hydrolysis of ethyl cinnamate in water-methanol media act as Entropy inhibitor and Enthalpy stimulator solvent. Such inference have also recently been supported by recent view of Singh A K [11]

TABLE II. THERMODYNAMICS ACTIVATION PARAMETERS OF THE REACTION IN WATER- ACETONE MEDIA ΔH^* AND ΔG^* IN KJ/MOLE, ΔS^* IN J/K/MOLE

% of MEOH	Mole %	ΔH^* in Kj/Mole	20^0C		25^0C		30^0C		35^0C		40^0C	
			ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$	ΔG^*	$-\Delta S^*$
30%	16.03	53.31	93.64	137.64	94.27	137.44	94.98	137.52	95.60	137.30	96.31	137.38
40%	22.90	52.95	94.20	140.78	94.91	138.42	95.65	140.89	96.31	140.77	97.03	140.83
50%	30.82	52.87	94.68	142.6	95.44	140.30	96.23	143.10	96.96	143.14	97.75	143.38
60%	40.06	51.28	95.16	149.76	95.88	147.24	96.72	149.96	97.43	149.83	98.23	150.00
70%	50.97	50.51	95.64	154.02	96.39	151.44	97.19	154.05	97.96	152.56	98.77	154.18

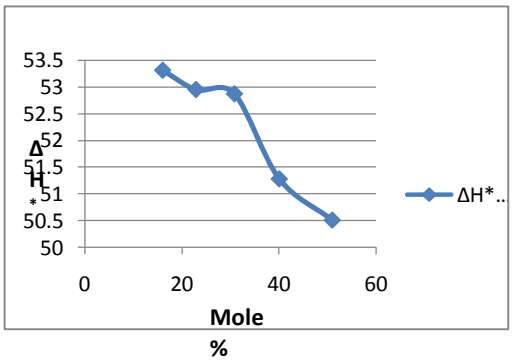

Figure 1. Variation of ΔH^* with mole % at 20^0c (water-methanol)

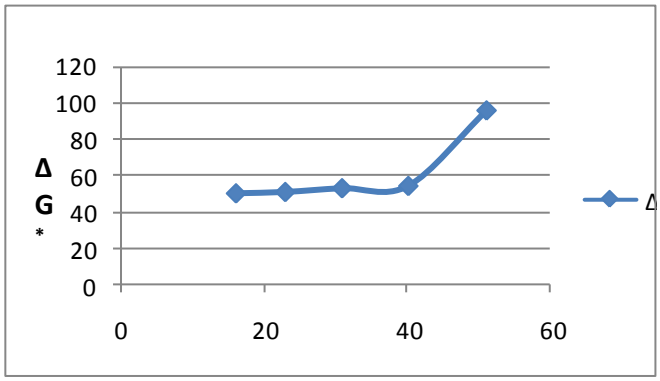

Figure 2. Variation of ΔH^* with mole % at 20^0c (water-methanol)

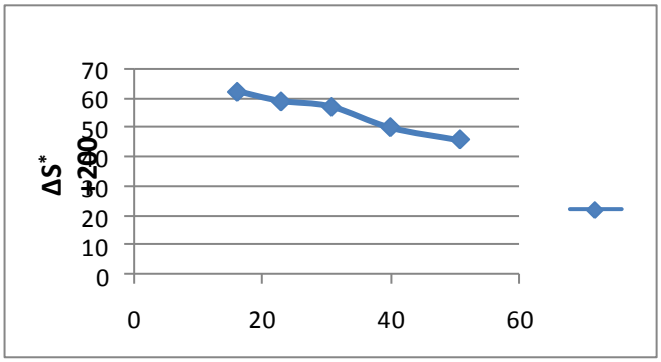

Figure 3. Variation of ΔS^*+200 with mole % at 20^0c (water-methanol)

C. *Evaluation of Iso-kinetic Temperature and Solvent-Solute Interaction*

In the light of Barclay [12] and Butler relationship between Enthalpy and Entropy of Activation, which is as follows?

$$\delta m\,(\Delta H^*) = \beta \delta m(\Delta S^*)$$

It is straight line equation representing the relationship between Enthalpy and Entropy of Activation. β is the Iso-kinetic temperature.

From the data available in the table II, the plot of ΔH^* and ΔS^* in both the solvent system in Fig. 4 and from the slope of straight line, the value of Iso-kinetic temperature was calculated to be 200 (water-Methanol) media.

From the value of Iso-kinetic temperature which is much less than 300, it is concluded that there is slow change in the structure of the reactant or in the solvent or in both due to weak interaction between solvent and solute present in both the reaction media in similar way as reported by Lefler [13]

Our this conclusion has been recently supported by Singh A K.[14]

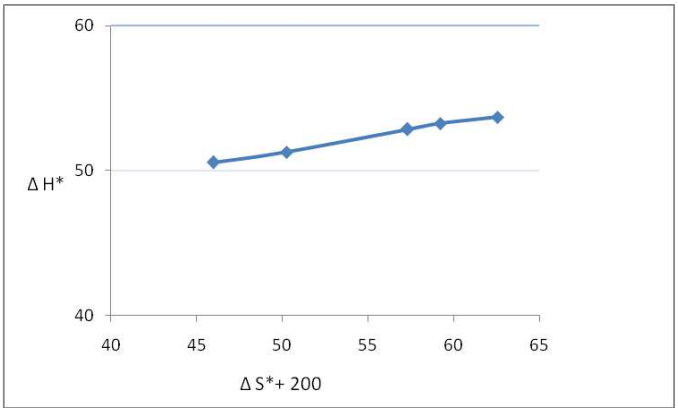

Figure 4. Variation of ΔH* with ΔS* at 25^0C (water-methanol) system

IV. Conclusion

The result of this work indicate that the rate of hydrolysis of Ethyl cinnamate, decreasing trend at all temp with increasing mole% of co-solvent which appear that transition state is more desolveted than initial state. The enhancement in the value of and ΔG^* with simultaneous decrease in ΔH^* & ΔS^* for the hydrolysis ethyl cinnamate in water- Methanol is enthalpy dominating and Enthalpy control. The Values of Iso-kinetic which is less than 300, clearly indicates that there is no appreciable interaction between solvent and solute present in the reaction media, i.e. reaction is not ion-dipole but ion-molecule type.

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AUTHOR PROFILE

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Breast Cancer Classification Enhancement Based on Entropy Method

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***Abstract*—Breast cancer is the most common form of cancer diseases among women and the second leading cause of cancer deaths worldwide. However, due to some limitations in mammography, it is difficult to classify a suspicious mass in the breast as malignant (cancerous) or benign. This paper attempts to classify the mammographic masses with high accuracy by combining entropy method with evolutionary algorithm (EA) and fuzzy logic. EA and fuzzy logic are applied at training phase for parameters tuning, however, entropy method is applied at training phase and localization phase, where at training phase entropy enhances indicator of fuzziness, while at mass phase entropy enhances EA for the classification of masses in mammogram images. The proposed method is evaluated by experimenting a number of the benchmark Mini-MIAS databases and the results shows better and more effective identification.**

Keywords-Breast Cancer, Evolutionary Algorithms, Fuzzy Logic, Entropy Method, Mammogram images and Feature Extraction)

I. INTRODUCTION

Breast cancer is one of the leading causes of mortality among women. It is expected that more than 26 thousand new cases among African American women to occur in US. The earliest sign of breast cancer is often an abnormality detected on mammogram screening. Early detection of breast cancer increases the possibility of recovery from the disease. Therefore, the most effective tool for detecting of breast abnormality, mammography screening have been used. Hence, for breast cancer classification, this paper presents a method by using EA, fuzzy logic and entropy method, where entropy method combine with fuzzy logic at training phase and with EA at mass phase and make the breast cancer classification process more efficient, robust and relatively fast.

II. RELATED WORK

A lot of approaches have been published in the literature for mammographic mass detection. A digitalized mammogram online and generates a high quality filtered segmentation of an image for biological interpretation and a texturefeature based diagnosis is needed. SVM model was regarded as an effective classifier and it showed good performances as compared with other classification models [1].

Besides that, SVM has been widely used for breast mammographic mass recognition. For example, Khan, et.al introduce and optimized Gabor filters with SVM classifier to recognizes the input ROI as malignant vs. benign[2]. The outcomes demonstrate encourage achievements of SVM against other models. The integration of SVM with PSO algorithm was discussed by Zyout etl.al [3]. In their work, hybrid of texture feature extraction techniques was implemented. By selecting the most effective texture features, the results that PSO able to reduce the complexity of the system has been indicated. Besides that, SVM was adopted for ROI mass classification in the work of Kanadam and Chereddy[4]. The main idea behind their work is to tackle the problem of mass shape variation. They introduce a new spares-ROI for shape representation and the outcomes show increase in the recognition performances. The synergy of SVM with Extreme Learning Machine (ELM) was studied by Lima et.al [5]. Convolution Neural Network (CNN) was employed in their developed scheme. Mainly, their CCNA-basedscheme consists of two cascaded layers i.e. low-level feature layer and high-level feature layer. The scheme was evaluated on a total of 600 mammographic images from DDSM database and the results indicate superior performances for the two-stage scheme over other single stage models. Additional work that integrates CNN with linear SVM was discussed by Arevalo et.al[6]. Extreme Learning Machine (ELM) based model was presented by Xie et.al [7]. In their paper ELM classifier was adopted with a set of texture features extracted from mass internal region, background region, and mass. The reported results show competitive achievements for ELM whoever inaccurate extraction of mass boundary will effect recognition performances. Besides SVM-based breast cancer diagnosis, there are a lot techniques have been developed such as Fuzzy c-mean based[8], Genetic based[9], Linear Discriminate Analysis (LDA) based [10],Artificial Immune based [11],AdaBoost based[12],and level-set based [13].

III. BACKGROUND

A. Evolutionary Algorithm

Evolutionary Algorithms (EA) are stochastic search and optimization heuristics, a subset of evolutionary computation as EA for generic population-based met heuristic optimization algorithm. Evolutionary computation techniques are optimization tools derived from the classic evolution theory of biological life in the natural world such as reproduction, recombination, mutation, and selection. An optimal solution is discovered by successively breeding generations assessed by an objective "fitness" function, which they are always working on whole populations of possible solutions for a given task.

For meeting a certain selection criteria, only those individuals of a population reproduce have been the basic idea, while the population of other individuals were died, for selecting the best meet of criteria, the population of those individuals have been converged. If imperfect reproduction is added the population can begin to explore the search space and will move to individuals that have an increased selection probability and that inherit this property to their descendants. These population dynamics follow the basic rule of the Darwinistic evolution theory [14]. The general EA process is shown in Figure 1.

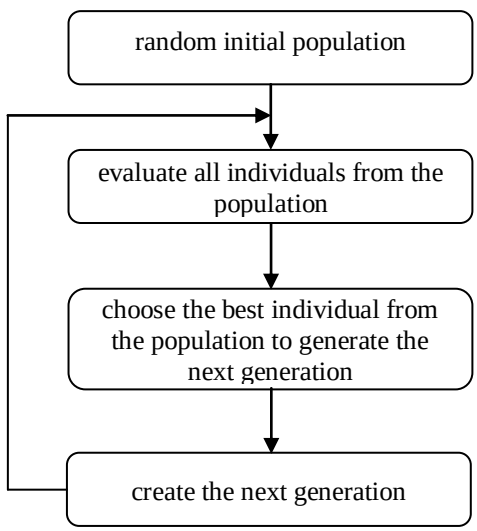


Figure 1. The general EA process

B. Fuzzy Logic

Fuzzy logic is based on fuzzy sets. In classical set theory there is a distinct difference between elements which belong to a set and those that do not. On the other hand, in the fuzzy approach, each element has a degree of membership to a set.

The main four types of shapes in Fuzzy Theory are Triangular, Trapezoidal, Gaussian (bell-shaped) and Singleton. On the other hand the general structure of Fuzzy logic system consist of four main components are fuzzification Interface, knowledge base, interface engine and defuzzification Interface as shown in Figure 2.

The fuzzy system designer must choose among several possible definitions of defuzzication. The two main methods of defuzzication: the method of the mean of maxima (MeOM) and the method of center of gravity (COG), where the COG defuzzication is more commonly used [15].

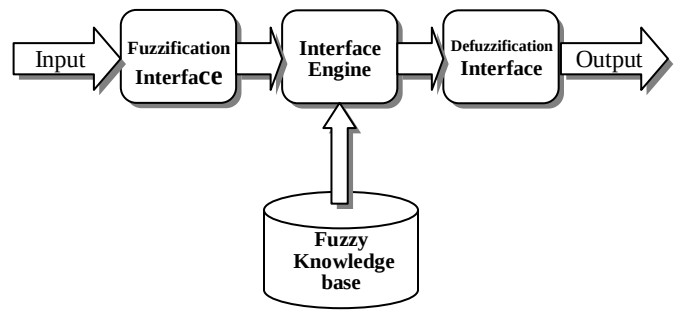


Figure 2. Overview diagram of a fuzzy system

C. Entropy Method

In information theory, Entropy is defined as the measure of uncertainty associated with a random variable. The term usually refers to the Shannon entropy, which quantifies - in the sense of an expected value. In other words, entropy is a measure of unpredictability of the state, or equivalently, of its average information content.

The Shannon entropy H(X) of a random variable X with probability mass function p(x) can be used to measure the average information content that is missing when the value of X is unknown [16].

Shannon defined the entropy for discrete variables as:

$$H(X) = \sum_{i=1}^{m} p_i . \log_2 \frac{1}{p_i} = -\sum_{i=1}^{m} p_i . \log_2 p_i \qquad (1)$$

where for given events $e_1, \ldots, e_m$ occurring with probabilities $p_1, \ldots, p_m$, p_i is equal to the chance of observing value i and $\log_2$ is the logarithm with base 2.

Shannon's entropy for an image can be computed such as a probabilistic method for comparing two pixels or a group of pixels and the probabilities of the gray level distributions. In evolutionary algorithm, entropy can disclose important information on EA parameters, where entropy can be used to indicate how influential a particular parameter is on EA performance. In Fuzzy logic, entropy method is used to conduct goal-driven calculations by processing the data that have been transformed into a fuzzy structure. Therefore, Fuzzy entropy is used to express the mathematical values of the fuzziness of fuzzy sets.

IV. Proposed Method

The paper presents a method for enhancement breast censer classification by combining entropy method with evolutionary algorithm and fuzzy logic. Entropy method is applied at training phase and localization phase, where at training phase entropy enhances indicator of fuzziness, while at mass phase entropy enhances EA for the classification of masses in mammogram images.

The proposed method consists of three stages as shown in Figure 3.The details are as follows:

Stage 1: The radiology marks the unknown mass with a square window as indicated in Figure 3.

Stage 2: Entropy method with evolutionary algorithm will be used to extract the features from the input window then a feature vector will be formed and presented to fuzzy logic classifier.

Stage 3: The trained entropy enhances indicator of fuzziness will recognize the input pattern as Benign (normal) or Malignant (abnormal) mass.

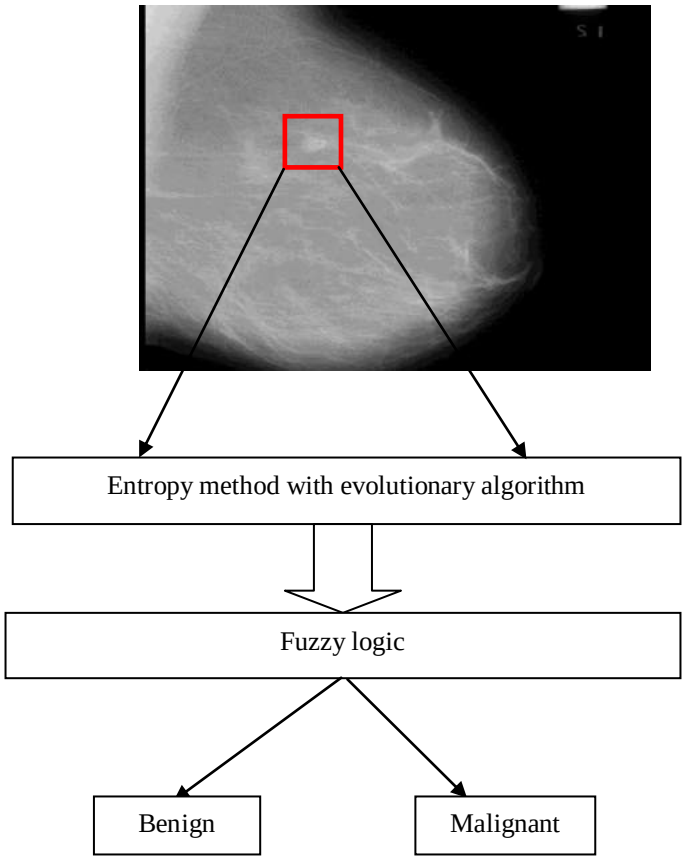


Figure 3.General View of Research Methodology

V. Experimental Result

A total of 500 DDSM images with 250 malignant ROIs and 250 benign ROIs have been used in this study. Moreover, a total of 1000 normal ROIs are employed. These normal ROIs have been generated randomly from various places inside the studied mammographic images. For evaluation purpose, each experiment was repeated ten times and the dataset was randomly split into three set i.e.40% training set, 40% validation set, and 20 % testing set respectively. The experimental analysis was conducted as follows.

A. *Entropy method for training phase*

The effects of the entropy method with respect to system performance, complexity, computational time were investigated. In the experimental study, the entropy method with fuzziness were used. Three performance indicators were computed, i.e. model complexity, computational time, and model accuracy. Each experiment was repeated ten times. The average and standard deviation of the performance indicators were computed.

Table 1: Analysis the effect of the number of classifiers on system perfomances

System	Accuracy (%)		Computational time (sec)		Complexity	
	Sensitivity (std.dev.)	Specificity (std.dev.)	Feature Extraction (std.dev.)	Recognition (std.dev.)	Total SVs (std.dev.)	Total Feat (std.dev)
1 classifier	84.75 (6.11)	30.93 (11.76)	1.84 (0.18)	0.03 (0.01)	65.0 (15.52)	210 (0)
2 classifiers	77.40 (4.89)	44.10 (5.09)	1.93 (0.16)	0.05 (0.01)	118.67 (9.71)	210 (0)
3 classifiers	72.88 (3.56)	64 (2.39)	1.95 (0.46)	0.06 (0.01)	201.40 (14.33)	210 (0)

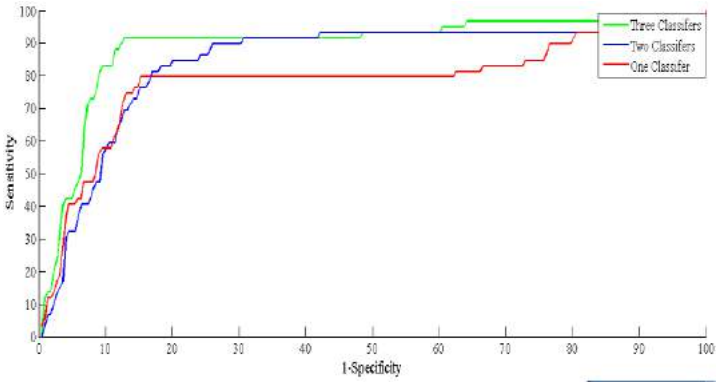


Figure 4: ROC curve results

B. Effects of the numbers of training features

The effects of the numbers of training features (F) and negative training instances (N) were investigated. In this section, the Centre Composite Design(CCD) technique was utilized to analysis the performances at three levels i.e. low, middle, and high. Accordingly, the F and N values were set at three different levels, i.e. low, medium, and high, as shown in Table 2.

Table 2: Parameters and levels of the CCD experiment

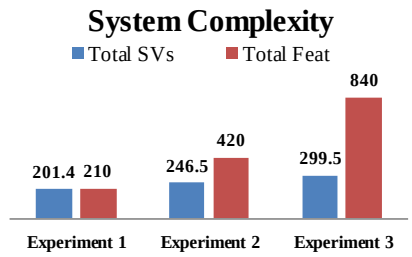
Parameter \ Level	Low	Medium	High
Number of features and negative Instances (*F*, *N*)	(5,10)	(10,20)	(20,40)

Each experiment was repeated ten times. The mean and standard deviation of the numbers of features and SVs, feature extraction time, recognition time, sensitivity rate, and specificity rate were computed, as reported in Table 3. The minimum model complexity in terms of the total number of features was achieved in Experiment 1. This was because the number of features and negative training instances were set to 5 and 10, respectively. However, when the number of features increased from Low to High, the feature extractions time increased. In addition, the recognition and specificity rate were improved by increasing the total number of features and negative training instances from Low to High, as shown in Table 3. These improvements resulted from the ability of the developed model to identify the true target patterns with higher numbers of features and negative instances.

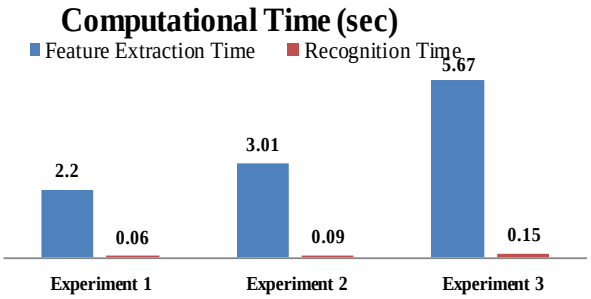
Table 3: Experimental results of parameter analysis

	Experiment 1 (Low)	Experiment 2 (Medium)	Experiment 3 (High)
Total Features	210.00	420.00	840.00
Total SVs	201.40	246.5	299.50
Feature Extraction Time (sec)	2.20	3.01	5.67
Recognition Time (sec)	0.06	0.09	0.15
Sensitivity (%)	72.88	62.97	51.67
Specificity (%)	64.00	70.00	78.07

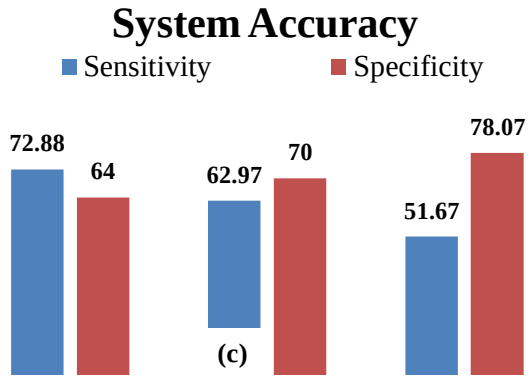
For graphical illustration, system complexity, computational time, and system accuracy are shown in Figure 5 It can be observed; that Experiment 1 produces the best sensitivity rate with minimum computational time of 0. 06 seconds recognition time, as well as the lowest degree of complexity with SVs of 204.40 and total features of 210.



(a)



(b)



(c)

Figure 5: Graphical view illustration
(a) System complexity (b) Computational time, and (d) System accuracy.

The Graphical User Interface (GUI) of the developed system is shown in Figures 6. To execute the system, two main steps are required i.e. ROI region labeling, and classifying the labeled region as Benign or Malignant as indicated in Figure 6 (b).

(a) (b)

Figure 6: GUI of the enhanced breast diagnosis system (a)-(b)

VI. Conclusion

This study encompasses the effect of entropy method for classifying the masses presented at mammographic images, which depend on Shannon's entropy concept. The developed system has been evaluated with a total of 500 DDSM mammographic images (250 malignant cases, and 250 benign cases). The reported results positively show a superior performance of the presented system over other variant methods. Additionally, from the statistical point of view, the proposed system was able to achieve significant results as compared with other models. Further work could be conducted by adopting the proposed model for different breast cancer images such as MRI and ultrasound.

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