Chapter 3
Methodology and Process Design

In this chapter, the designation of an UVO surface treatment system and method, particularly, for continuous fiber-reinforced composite manufacturing was proposed. In order to verify and evaluate the effectiveness and feasibility of the designated system for applying in the industrial, the experimental methodology for studying the effects of UVO process on the mechanical properties of the composites was also included. A disadvantage of the UVO treatments of the prior works [cf. 2.12] is that they are non-continuous process. Those batch processes are time consuming and sometimes unreliable. In contrast, for mass production of the composites it is preferably to continuous process such as pultrusion and filament winding. There is a need for development of an environmentally friendly as well as cost effective and robust surface treatment process which can be used over a range of polymeric surfaces. It is therefore an objective of the present designation to provide a preliminary process and equipments for industrial, which are reliable and can produce a highly active surface to improve adhesion with the continuous phase (matrix) in composite system.

3.1 Materials

In this study two main constituents used in the production of the specimen were epoxy matrix and polyethylene terephthalate (PET) yarns. Basic knowledge and specific data of the materials are detailed below.

3.1.1. Epoxy Resin

In this study epoxy resin and hardener were supported by Thai Epoxy and Allied Products Co., LTD. Code name of the resin and hardener were EPOTEC YD-582 and XDH-125, respectively. The resin is a low viscosity modified epoxy. It has a very good wet out, degassing properties, and an excellent adhesion to reinforcement. EPOTEC YD-582 with the hardener XDH-125 is ambient temperature cure system. This system can be used in wet lay up lamination, resin transfer molding (RTM), pultrusion, filament winding and etc. Typical data of the resin and hardener are shown in tables below [54].

Table 3.1 Typical properties of EPOTEC YD-582

Property	Test method	Unit	Specification
Appearance	-	-	Clear Liquid
Epoxy Equivalent Weight	DIN 16945/4.15B (89)	g/eq	180±5
Viscosity at 25 °C	JIS K 7233 (86)	cPs	1500±200
Color	ASTM D-1544 (89)	Gardner	MAX. 0.5
Density	TEC-AS-P-004	g/cm³	1.15-1.16

Table 3.2 Typical properties of EPOTEC XDH-125

Property	Test method	Unit	Specification
Reactivity	-	-	Standard
Appearance	-	-	Pale Yellow
Viscosity at 25 °C	JIS K 7233 (86)	cPs	250±50
Density at 25 °C	TEC-AS-P-004	g/cm³	1.07-1.08

Table 3.3 Typical Handling properties of EPOTEC YD-582/XDH-125 mixture

Property	Unit	Value
Resin : Hardener Ratio	-	3:1
Pot Life @25 °C (100 g Mix)	min	20±2
Gel Time with 1-8 Layers of Glass Fabric @25 °C	min	135±15
Time to Achieve Good Strength with 1-8 Layers of Glass Fabric @25 °C	min	210±30
Exothermic Temperature	°C	85±5
Glass Transition Temperature, T_g	°C	70±5
Post Curing Condition to Achieve Optimum Strength @ 40 °C @ 60 °C @ 80 °C	Hour	18 9 3

3.1.2. Polyethylene Terephthalate (PET) Fiber

The fiber samples used in this study was PET yarn for sewing thread. Each filament had an average diameter of ~ 10 μm. All the fiber samples were not attempted to clean nor dry before use in the UVO treatment process. Figure 3.1 shows SEM micrograph of the PET spun yarn used in this study.
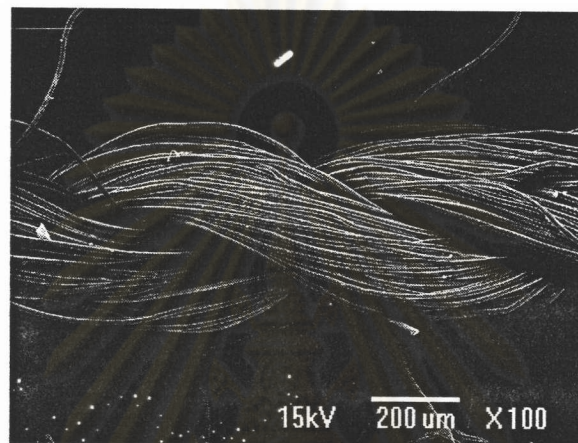

Figure 3.1 SEM micrograph of the PET spun yarn

3.2 Methodology

Prior to the process and equipments design, the experimental methodology must be clarified. To obtain reproducible and reliable results and to meet an agreement of hypothesis and conclusions, the experimental design must be systematic and respect to scientific method. The aim of this research work, however, was emphasized on mechanical properties of resulted composites (PET/epoxy), not on the fiber itself (PET). One more criteria to specify the methodology of the experiment is the applicable of this technique to scale up for industry. Figure 3.2 represented the experiment methodology.
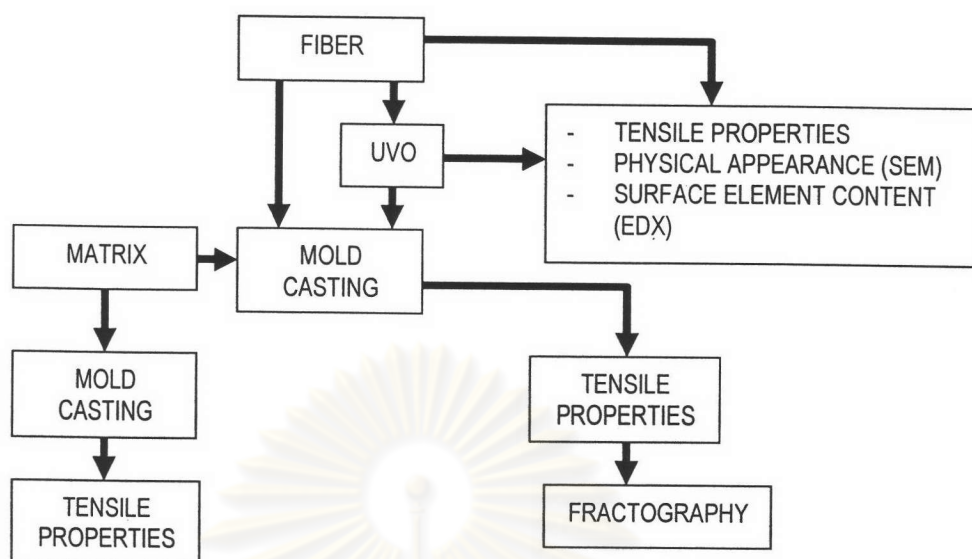
Figure 3.2 Schematic diagram of the experimental methodology.

From Figure 3.2, to determine the effects of UVO treatments on the tensile properties and physical appearance of fibers (PET yarns), the universal testing machine (UTM) and scanning electron microscopy (SEM) were used (both before and after UVO treatment). The tensile test was also carried out with the as-received matrix (epoxy) to compare the tensile properties of the material whether or not incorporated with the fiber.

To investigate effects of gas species on the UVO treatments, the reaction conditions for each of the treatments are listed below.

- UV/N_2: Nitrogen gas (inert gas) was used to study the effects of UV light in absence of ozone or oxygen environment. The dry nitrogen flow rate was 4720 sccm (standard cubic centimeter per minute) or 10 scfh (standard cubic foot per hour).

- UV/O_2: The ozone was absent in the reactor. The dry oxygen flow rate was 4720 sccm.

- UV/O_2+O_3: The incoming oxygen gas to the reactor was pretreated in the ozone generator so it had significant quantities of ozone. The dry oxygen flow rate was 4720 sccm.

- UV/air: The unconditioned air was fed to the reactor. This regime was used to study the feasibility to reduce operating-cost of the process. Since in air oxygen gas content is approximately 21 %, the flow rate of air feeding was reduced to 2360 sccm or 5 scfh.

- UV/air+O_3: The incoming air to the reactor was pretreated in the ozone generator. The air flow rate was 2360 sccm.

To determine the effects of exposure time or rate of surface modification, the samples were treated for 2, 5, and 10 minutes under the above conditions. The reactor was designed to operate in continuous mode which can eliminate any effects attributed to unstable conditions in the reactor before equilibrium was reached. The reactor was allowed to stabilize before introducing the samples (continuous yarns) into the reactor. Exposure times and stable condition in the reactor were achieved by employing a speed-adjustable driving unit which allowed us to start/stop and varying speed of samples introducing into the reactor.

Since, in this study, only effects of exposure time and gas species were examined, other parameters were carefully controlled such as temperature, pressure, gas flow rate, ozone concentration and humidity. Any contact to the surface of the fiber samples before and after treatment should be avoided. Treated samples must be safely kept in zip-lock bag and avoided to expose them to strong sunlight and other light sources.

Composites of treated and untreated fibers were fabricated by pouring the mixture of epoxy resin and hardener in to the casting mold. This step was done by carefully align the fibers with an attempt to avoid any damage to the fiber surface, which can be occurred when the fiber made contacted or rubbed against the stainless steel mold. Fabrication of the composites must be done as soon as possible (with in 24 hrs.) to avoid aging effect. The resulted thermosetting-matrix composite must be stored until curing was completed (7 days), then the tensile properties can be tested. Tensile test of the composites was followed the ASTM standard method number D638M-91a. The tensile test of the fiber samples was followed the ASTM standard method number D3379-75. However, further details of the experiment procedure will be discussed later in the next section.

3.3 Process Design and Construction

After literature survey was completed (cf. 2.12), during the early stage of the design, the process flow diagram of the overall process has to be established to show the sequence of equipments and unit operations. To simplify visualization of the unit operation, Figure 3.3 presented the schematic of the qualitative flow diagram of the UVO process.
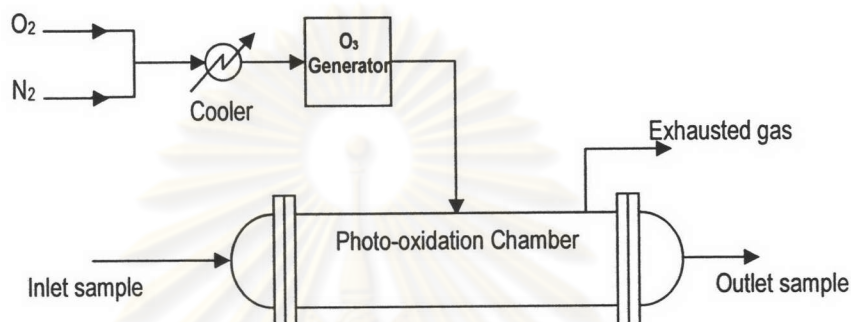

Figure 3.3 Schematic of the qualitative flow diagram of the UVO process.

In addition to the flow diagram, process layout and the equipments within the process must be planned before detailing piping, structural, and electrical design. CAD (computer aid design) and three-dimensional modeling software are useful techniques for making rapid and accurate layout. In this project, AutoCAD® 2002 (AutoDesk Inc.) and 3ds max 5 (AutoDesk Inc.) were used for determining the appropriate location of the equipments and facilities. The first software was a powerful tool for scale-drawing while the latter was beneficial for three dimension rearrangement of the process (in this project the latter was not used for scaled-drawing). The 3ds max program can be render 3D modeling and enable to specify a characteristic of material to the drawing, such as metal and glass, which the 2D scaled-drawing can be imported from AutoCAD. Figure 3.4 and 3.5 shown the samples of screen captured pictures and graphical results from AutoCAD and 3ds max, respectively.

As shown in Figure 3.5b, fibers (2) were introduced from fiber creels (1) through the fiber guide (4) prior to enter into the reactor chamber (6) by pulling mechanism (8), and then stored in the spools (9). Gases (O_2 and/or N_2) were introduced from the gas tanks (3) passing through an ozone generator (5) to generate ozone and then to the reactor chamber. Exhausted gases were allowed to exit the chamber via the exhausted outlets (7).
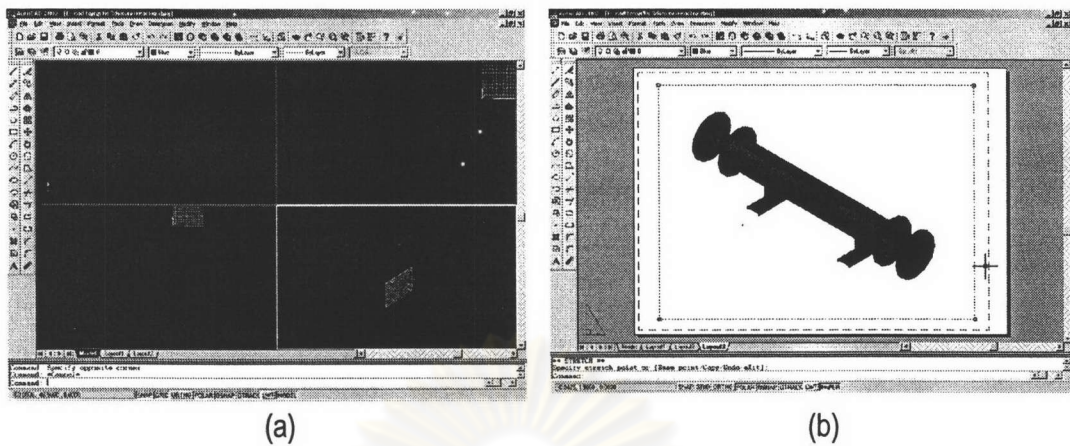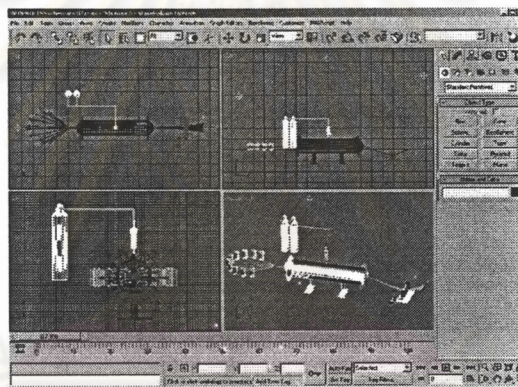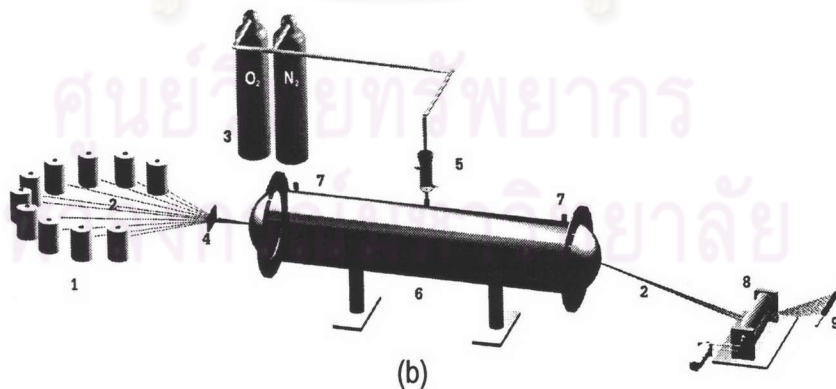
(a)   (b)

Figure 3.4 2D and 3D scaled drawing and model created by the AutoCAD® 2002 software. (a) The veiwports display of scale drawing of the reactor chamber and (b) rendered model shown the scaled reactor chamber and lids (more details of the equipment design and sizing were shown in the next section).

(a)

(b)

Figure 3.5 A schematic rearrangement of the equipments created by the 3ds max® 5 software. (a) The viewports display of rearranged equipments with in UVO process of this study and (b) rendered model of overall UVO process.

3.3.1 Equipments Design and Construction

In accordance with objectives of the experiment, an ultraviolet-ozone surface photo-oxidation system included;

(1) sources of ultraviolet light

(2) reaction chamber

(3) ozone generator for generating and delivering ozone to the reaction chamber

(4) pulling mechanism for continuous delivering samples in and out of the reaction chamber

(5) monitoring devices e.g. temperature measurement unit, pressure gauge, and volumetric gas flow meter

(6) pictures-frame casting mold for fabricating a composite dumbbell-shaped specimen

Each components of the unit design required careful consideration of materials (chemical resistance, physical properties, reflectance to UV), geometry (ozone concentration, temperature and UV intensity gradients), operating conditions (fiber speed, gas flow rates) as well as safety factors.

3.3.1.1 Selection of Ultraviolet Light Sources and Construction of Lamp Control Unit

There are several types of ultraviolet light sources commercially available in the market. The major type of ultraviolet lamp is mercury vapor arc lamps which are fall in to three main categories:

(a) Low pressure: operate at about 10^{-6} bar at room temperature (1 bar = 0.987 atmosphere)

(b) Medium pressure: operate at about 1 bar at room temperature

(c) High pressure: operate at about 100 bar at room temperature

To select an appropriate lamp to use in the experiment some specifications such as emission spectra (which are different for low, medium and high pressure lamps), intensity of emitted radiation, working temperature, life time, size and construction are required for consideration to meet an agreement of the design objectives.

The output of the low-pressure mercury vapor discharge lamp is limited to various lines in the emission spectrum of mercury. The main lines are at 184.9 nm and 253.7 nm. The line at 184.9 nm is the most intense since it is freely allowed by the selection rules. However, it is less intense than that at 253.7 nm outside the lamp, owing to absorption by the quartz envelope. In some cases the line at 184.9 nm is totally blocked by phosphor doping.

Although the line at 253.7 nm is not permitted by the selection rules, since it involves a triplet-singlet transition, which are normally of low probability but it does in fact occur with mercury. Due to its low-pressure condition, collision or some other perturbing factor are not aid in emission process, these lamps are essentially free from continuum and therefore are often employed as sources of monochromatic radiation of wavelength 253.7 nm [55, p.42]. In the low-pressure mercury lamp most of the radiation (> 90%) is concentrated at 253.7 nm. This 253.7 nm radiation is the most significantly in UVO process.

There are two chief types of low-pressure mercury arcs. These are hot cathode and cold cathode. Hot-cathode electrodes need a high temperature for electron emission. These thermionic lamps have the disadvantage that the electrodes are in part consumed during start-up. In contrast, the cold-cathode electrodes are not consumed and they therefore have longer lifetimes, however, they are more expensive than those hot-cathodes.

In this project, the Phillips TUV TL-30W low-pressure mercury lamps were selected. These lamps actually are for germicidal purposes. Since they are almost monochromatic emission at 253.7 nm, this wavelength has enough energy that can expect some bond ruptures to be caused in non-photo-initiated irradiated systems (if the molecule absorbs the radiation), in particular with a high-intensity. Moreover, the lamp has a cheap price compared with another UV sources, therefore this lamp model is suitable for our economically UVO surface modification process.

Phillips TUV TL-30W low-pressure mercury lamps consist of a tubular glass envelope, which can filtered out the 184.9 nm ozone-forming line. Electrodes of the lamps are hot-cathode type. Four lamps were used in this study to increase the intensity. The manufacturer's stated warranty for useful life of the lamp is 8000 hours to 85% of the original 253.7 nm output irradiance. In Figure 3.6, a photograph, dimensions and its emission spectrum of the Phillips TUV TL-30W lamps were shown.
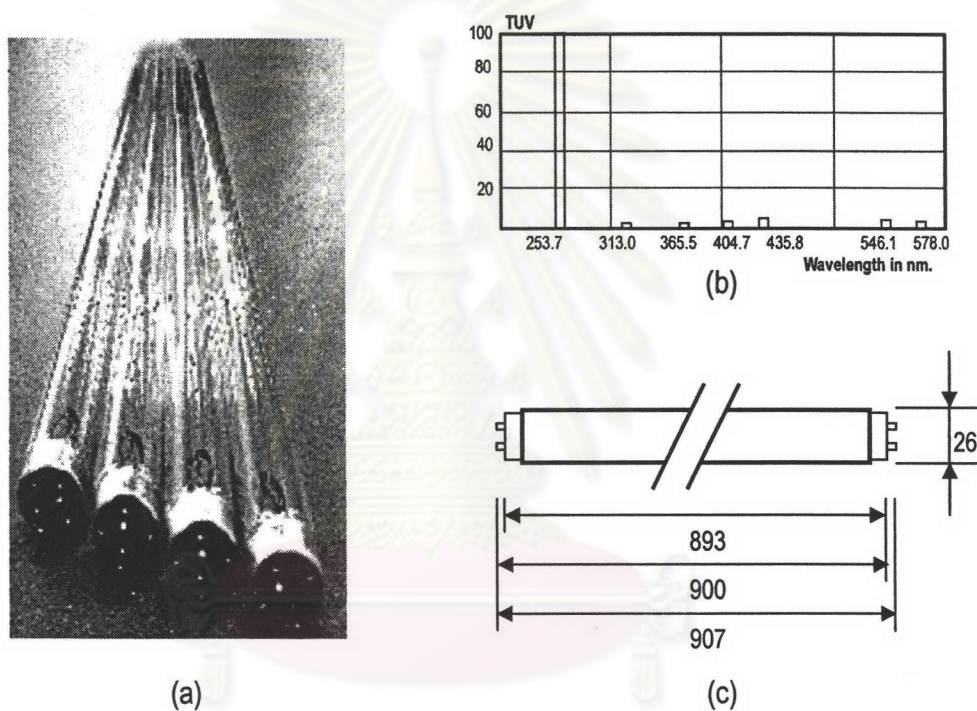

Figure 3.6 Photograph (a), emission spectrum [56] (b), and dimensions in millimeter (mm) (c), of the selected Phillips TUV TL-30W lamps.

Emission is started from low-pressure mercury lamp by applying a voltage across the two electrodes causing ionization of the starting gas. This produces current flow and develops into an electric arc. The working voltage depends on tube length and is generally of the order between 240V and 200V AC.

Mercury vapor tubes do not obey Ohm's law. They have a voltage/current characteristic which is negative and non-linear. As the arc intensity increases, so the electrical resistance goes down and, without input power control, the ever increasing current would inevitably destroy the tub. For this reason a constant-wattage ballast unit comprising predominantly positive series impedance was used to supply each tube.

The emitted intensity from an arc may be sensitive to current density flowing through the arc. In the case of low-pressure mercury arcs producing the 253.7 nm line, the intensity is at low current values linearly proportional to the current.

In this project, to construct the UV lamps unit, four low-pressure mercury Phillips TUV TL-30W lamps were connected in parallel configuration, while ballasts were connected to each lamp in series.

Switches and starters were also connected to each lamp, allowing electricity and initiating operation to the lamp. Each lamp can be operated, i.e., to turn on/off, separately. All of lamp controlled devices included switches, ballasts and starters were install in an aluminum box which was isolated from the UV lamps located in reactor chamber. Insulated electric wire and connectors were used to connect UV lamps inside the reactor with the controller box. In Figure 3.7 the lamp controller box, accessories and configuration diagram of the UV lamps unit were illustrated.
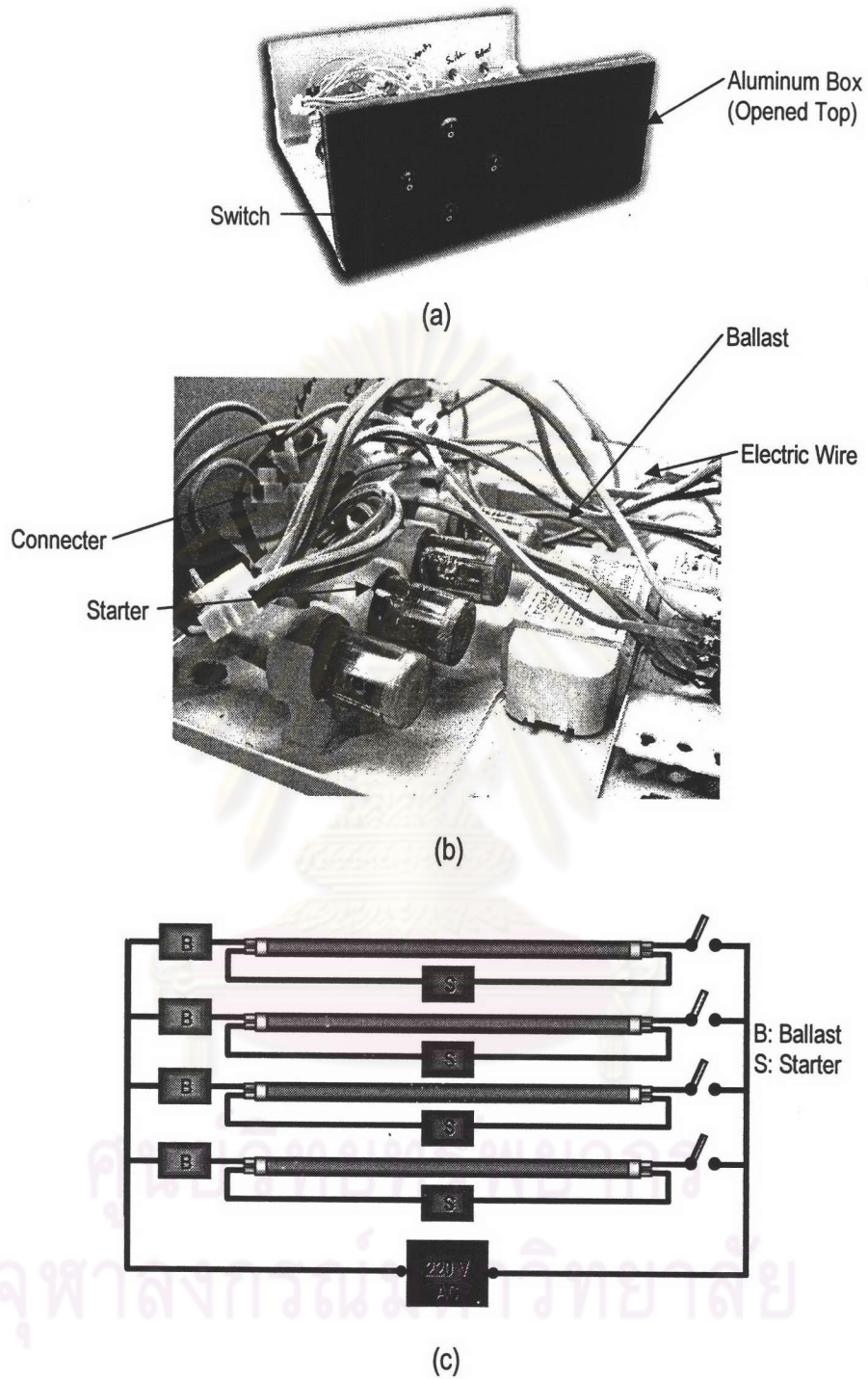
Aluminum Box
(Opened Top)

Switch

(a)

Ballast

Electric Wire

Connecter

Starter

(b)

B: Ballast
S: Starter

(c)

Figure 3.7 (a) Controller box, (b) lamp controlled devices included switches, ballasts and starters and (c) configuration diagram of the UV lamps unit.

3.3.1.2 Reactor Chamber Design and Construction

After selecting the UV source, reactor chamber was the next to be designed. In this work, the reactor chamber where all the reactions taking place must be functioned as:

1. Gases vessel: to isolate system from external environment, keeping a stable and controllable condition (temperature and pressure) of the reactions
2. Lamp holder: for holding UV lamps into certain position
3. Samples guidance: to align samples in continuous form so that the samples can get a uniform environment
4. Shielding and UV reflectance: to give no stray radiation leakage and efficiently reflect the UV light to increase effectiveness of the process

Concepts of the reactor chamber design were fallen into two aspects, material and operation functions. In case of material aspect, the material used to construct the reactor chamber required some special properties such as chemical resistance, i.e., it should be possess adequate chemical resistance to prevent corrosion caused by ozone, high reflective index to UV light, and ease of construction, cleaning and maintenance. For another aspect, the reactor geometry must perform a constant UV intensity during operation, high productivity or high production rate as well as safety for operation. Computer aid design programs were used again in drawing and designing of the parts.

In this work, 3.175 millimeters (0.125 inches) thick stainless steel sheet (type 304) was chosen to construct the reaction chamber. This is because stainless steel possesses excellent oxidation corrosion-resistance [57, p.423] as well as good reflection to UV radiation of about 60% [55, p. 49]. The chamber was constructed by rolling and welding the stainless steel sheet into tubular shape. Inside diameter of the tubular is 152.4 mm (6 in.) and the length is 1000 mm (39.37 in.).

The eight holes drilled flanges were made and welded to both ends of the tubular for attaching the tubular with lids. To avoid any existing of dead-zone in the chamber, two hemisphere shaped lids were made by pressing stainless steel sheet. The lids were also drilled into 8 holes. Doughnut-shape rubber seals were attached to the lid's flange to prevent gases leakage. Nuts and bolts were used to attach the flanges to both ends of the tubular part. Two stands were attached to the tubular chamber to keep the chamber in horizontal.

Interior of the tubular part and lids were polished to give a higher reflection to UV light. Lamps holders were located inside the chamber to fix all four UV lamps in horizontal and also perpendicular to each other. Each hemisphere lid was drilled a very small hole ($\varnothing$=1 mm) on the top, these holes were used for introducing the continuous fiber into and out off the chamber.

Introducing of gases species was split by using three inlets located at the middle and 20 cm from both ends of the tubular chamber, whilst the gases were allowed to exit the chamber through the two small drilling holds on the lids. The inlet gases were spitted into 54 flows along the reactor chamber by flow nozzles. The gases species were forced to pass through the center of the reactor chamber, where the samples were mounted in during passing through the chamber, to give an increasing of collision of gases molecule to the sample's surfaces.

The power supply connections for the UV lamps were also mounted at both ends further away from the gas inlet pipe connections. Opposite direction to the gas inlet pipe connections of the reactor chamber a 10 mm diameter drilled hole was prepared for attaching the temperature sensor. Figure 3.8 and 3.9 shown drawings and photographs of constructed reactor parts.

a) ∅ 10 mm gas inlet
b) ∅ 10 mm pressure gauge socket
c) ∅ 10 mm electric connection
d) stand
e) tubular chamber
f) lid
g) UV lamp
h) seal rubber
i) ∅ 1 mm drilled hold
j) ∅ 8 mm drilled hold
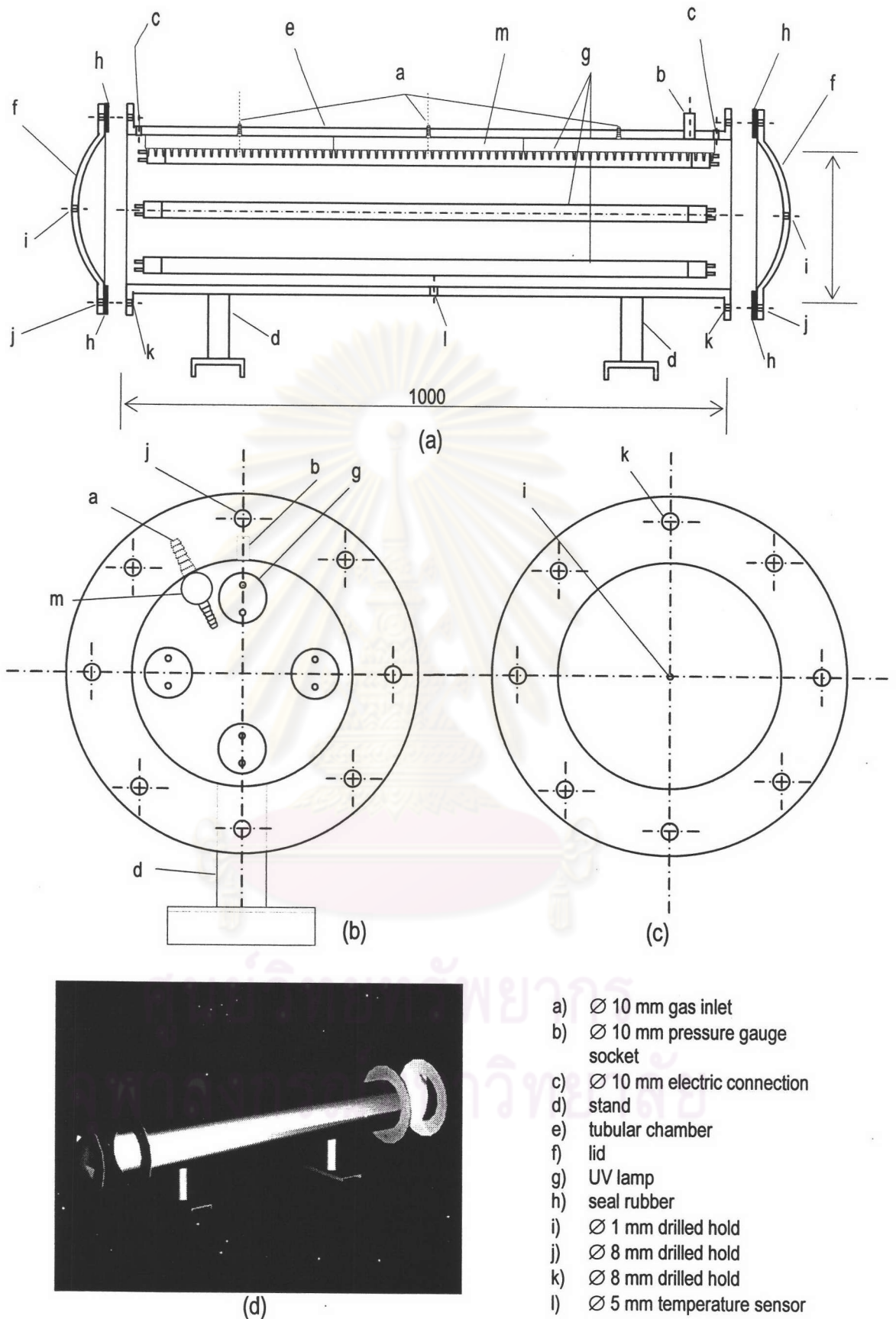k) ∅ 8 mm drilled hold
l) ∅ 5 mm temperature sensor

Figure 3.8 Design of the reactor chamber (not drawn to scale). (a) Cross-section front view and dimensions in millimeters of the reactor, (b) side view of the reactor (no lids included). (c) lids, and (d) three-dimensional model of the reactor.
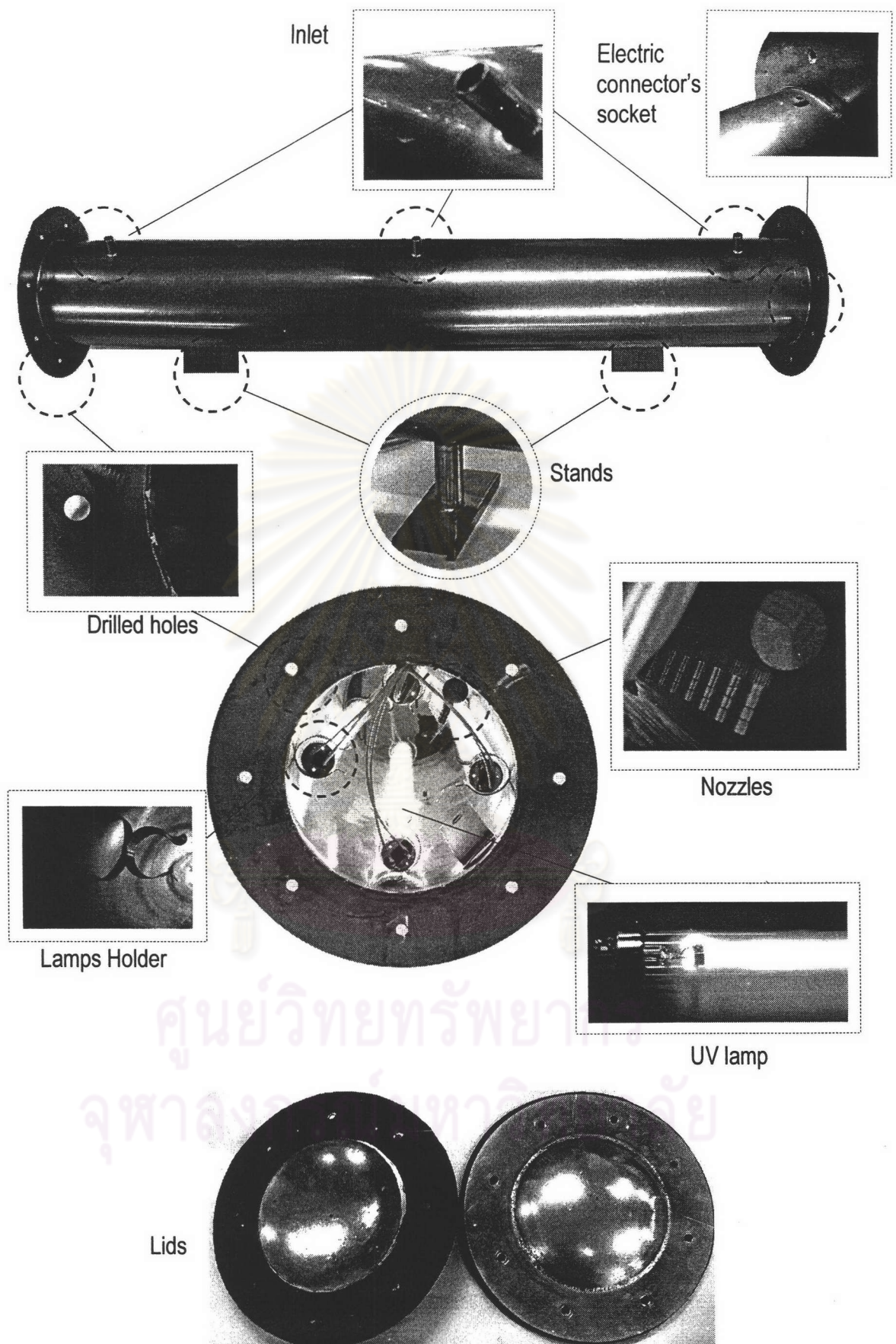
Inlet

Electric connector's socket

Stands

Drilled holes

Nozzles

Lamps Holder

UV lamp

Lids

Figure 3.9 Photographs of constructed reactor chamber.

3.3.1.3 Ozone Generation Design and Construction

Ozone is an allotrope of oxygen, comprising a molecule of three oxygen atoms (O_3). It is highly unstable and a strong oxidant, which makes it useful for water purification, room sanitation, equipment sterilization, food preservation [58] and, of course, surface modification, as it spontaneously oxidizes many compounds. The physical properties of ozone were listed in Table 3.1. Ozone has a half-life of only about 22 minutes at ambient temperature (and about 2 hours in water) [59], and at higher temperatures the rate of ozone decay is accelerated. Ozone cannot be stored for practical purposes. This is also an advantage, as ozone rapidly decays away to safe levels.

Its readiness to decompose makes ozone a powerful oxidizing agent capable of initiating violent chemical reactions. The materials of construction for equipment to contain ozone must therefore be chosen with great care. Glass, stainless steel, aluminum, polyvinyl chloride and polyethylene are among those considered acceptable [60].

Ozone is generally formed by the action of oxygen atoms (O_1) on oxygen molecules (O_2). The splitting of the oxygen molecule can be achieved by applying electrical, optical, chemical, or thermal energy to the oxygen molecules. Most optical methods use ultraviolet radiation. Generally a special lamp inside an ozone chamber radiates ultraviolet light of wavelength at 185.9 nm which converts oxygen molecule (O_2) into active oxygen (O_1) and ozone (O_3) molecules. However, ultraviolet radiation methods produce ozone in only minimal concentrations which are in many cases insufficient for a particular application. In addition, Ultraviolet UV lamps are bulky, so that an ultraviolet ozone generator cannot be very compact.

Ozone may be produced by passing an oxygen (O_2) containing gas through a high voltage discharge or corona. A corona discharge is a discharge of electricity within the gaseous dielectric (for example air) along the surface of and between the conductors or electrodes. The structure of a corona discharge device, two conductors separated by a dielectric (gas) is similar to that of a capacitor. The corona discharge, which appears as a bluish-purple glow, is due to the ionization of the insulting gas between the electrodes. This discharge occurs when the field potential gradient of an alternating current exceeds the corona start or threshold voltage and continuous until the voltage is reduced or stopped. The field potential gradient is the voltage per unit length along the conductive part of the device.

For producing ozone, an oxygen containing gas is supplied as the insulating gas between the conductors (i.e. into the corona field). This causes some of the oxygen (O_2) molecules bond to split, freeing two ionized oxygen atoms which create ozone when colliding with other oxygen molecules and/or with other ionized oxygen atoms. It is usually necessary for the oxygen containing gas to be dried, and it is also advantageous for the gas to be cooled. The most readily available gas for this purpose is air. However, a more concentrated source of oxygen can also be used. The ozone/gas mixture discharged from corona discharge ozone generators normally contains from 1% to 3% ozone (by weight) when using dry air, and 3% to 6% ozone (by weight) when using high purity oxygen as the feed gas [59].

Table 3.4 Physical properties of ozone [60, p.2].

Molecular weight	47.998 g mole^{-1}
Boiling point	-111.3 °C
Melting point	-192.5 °C
Density, gas at 0 °C, 760 mm Hg (1 atm)	2.14 kg m^{-3}
Density liquid	1352 kg m^{-3}
Maximum in the absorption spectrum for the gas in the UV region	254.7 nm
1 ppm by volume in air at 25 °C, 760 mm Hg (1 atm)	Equivalent to 1.96 mg m^{-3} or 1.5 ppm by weight

A solid dielectric material, in addition to the gaseous dielectric, is usually included between the two electrodes or conductors to prevent shorting between the electrodes and to intensify the electric field. The solid dielectric may be plastic, ceramic, or glass, for example. The solid dielectric is gapped or spaced from at least one of the electrodes to allow for space for the air or feed gas to flow through the corona region. For structural simplicity, in many devices the solid dielectric aligns or runs along one of the conductors while being spaced from the other.

One drawback of corona discharge units is that when air is used as the insulting gas, there is a potential danger that some of the high composition of nitrogen, N_2, (78% in air) may ionize and break into singlet atoms which react to form nitric oxide (NO), nitrogen dioxide (NO_2) or nitrous oxide (N_2O). Formation of these compounds inhibits the ozone generation process. This potential problem is heightened when there is a substantial amount of water vapor in the air and when the applied electrical voltage is very high.

In this work, three corona-discharge ozone generators were used (shown in Figure 3.10). The generators are cylindrical-type with outer diameter of 30 mm. The feeding gas was forced to flow parallely through the identical axial of two cylindrical electrodes. All three ozone generators were connected parallely. Feeding gas from gas tank was split into three equal parts which flow to the generators. The ozone-contained gas mixtures were then combined and split again into three inlets of the reactor chamber. Electricity and tubing connections diagram of the ozone generators is illustrated in Figure 3.11.
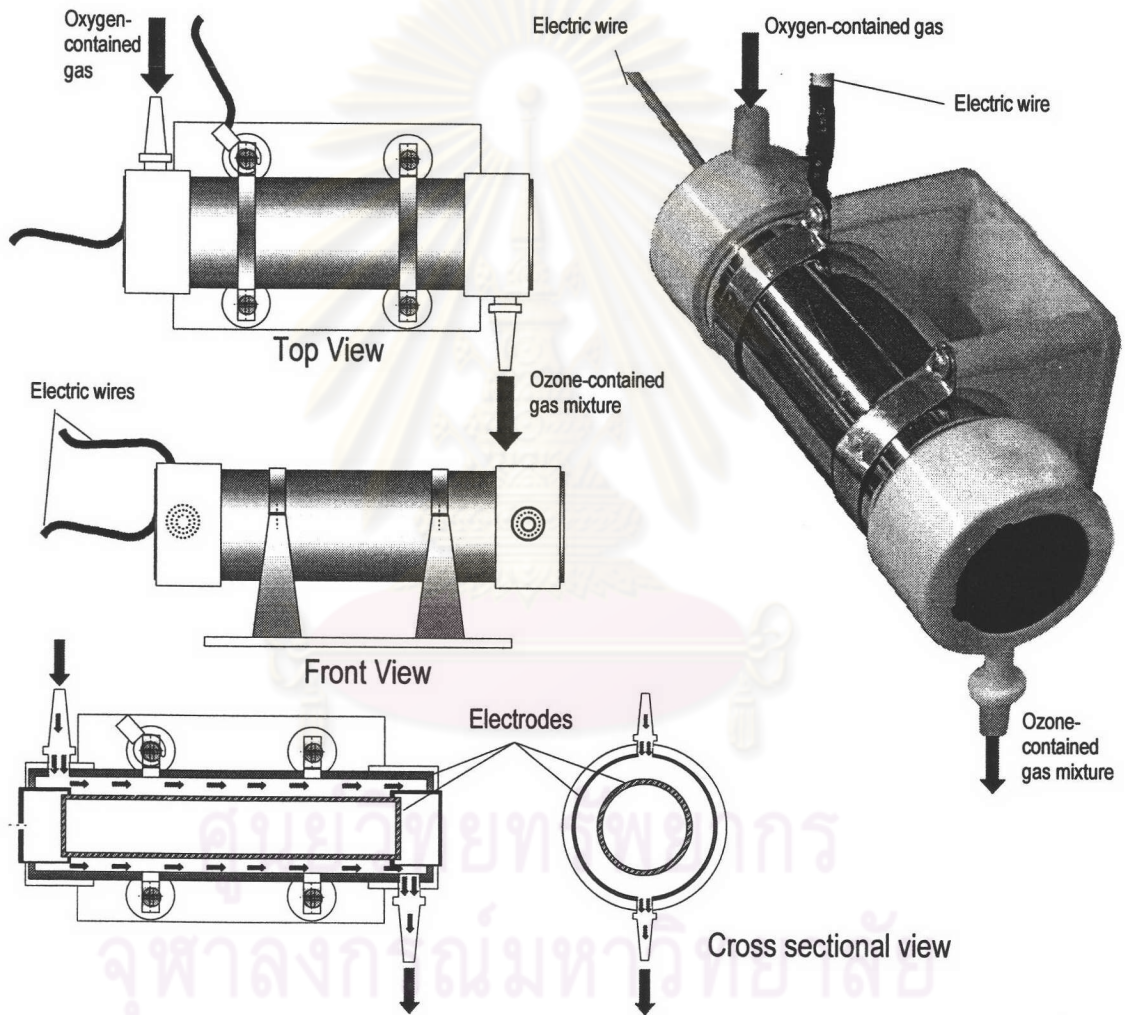
**Figure 3.10** The ∅ 30 millimeter cylindrical ozone generator.
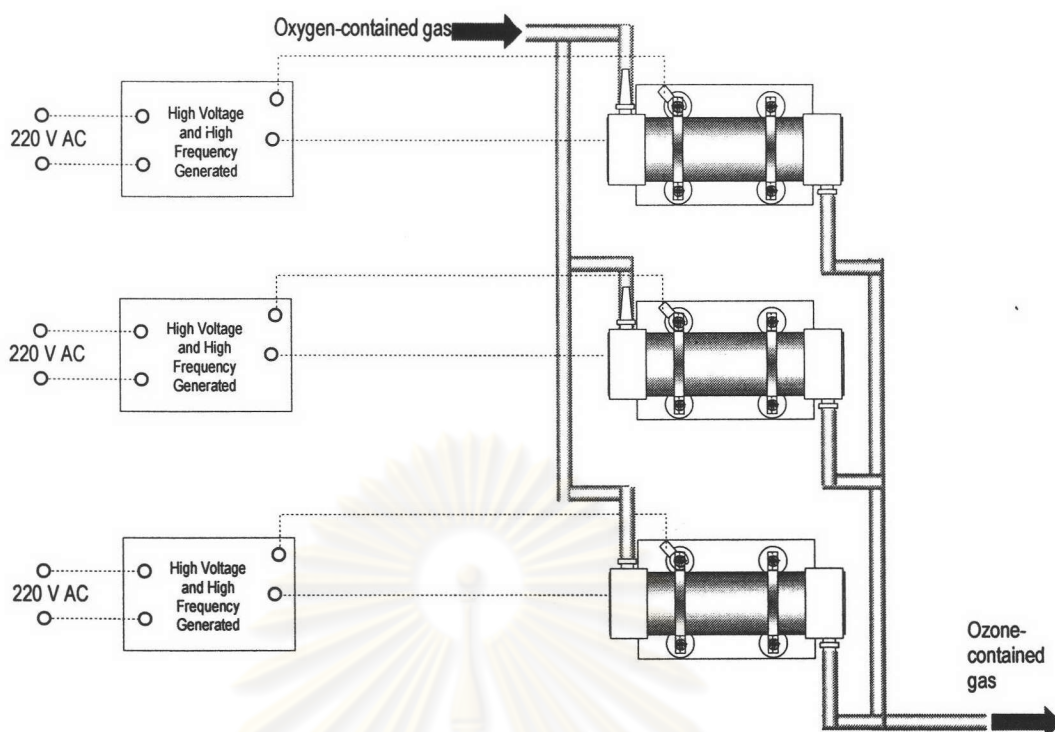
Figure 3.11 The diagram of parallel ozone generators connection of electricity and tubing.

The rate of ozone generation was examined by iodometry titration. Oxygen/ozone gas mixture from the three ozone generators was allowed to flow through two Erlenmeyer flasks containing 400 ml of 2% potassium iodide (KI) aqueous solution in each of them, as shown in Figure 3.12. A diffuser was attached to the end of tubing in order to get small bubbles of ozone so that a large number of ozone can be absorbed by KI solution. Both KI solution flasks were connected in a series so that unabsorbed ozone from the first flask could be transferred and further absorbed in the second flask. The ozone containing gas was bubbled in the KI solution at a flow rate of 20 scfh (standard cubic foot per hour) for 3 minutes. The reaction of ozone with KI released iodine (I_2) which is determined by titration using sodium thiosulphate solution (Equation 3.1). The amount of ozone produced by the generators could be calculated by the consumption of sodium thiosulphate solution.

$$2KI + O_3 + H_2O \longrightarrow I_2 + O_2 + 2KOH$$
$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

(3.1)
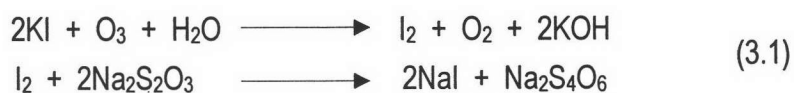
Titration of the ozonated KI solutions required acidification the 40 ml of the solution with 1 ml sulfuric acid (H_2SO_4). After acidification, the iodine in the KI solution was immediately titrated a 0.2 N sodium thiosulphate solution. This process was followed by the addition of 1 ml of the starch indicator solution to the tritrant just before the end point was reached. The consumption of sodium thiosulphate is needed to calculate and determine the ozone concentration. The assembly for a Standard Iodometry Method for ozone product-gas measurement is shown in Figure 3.12.
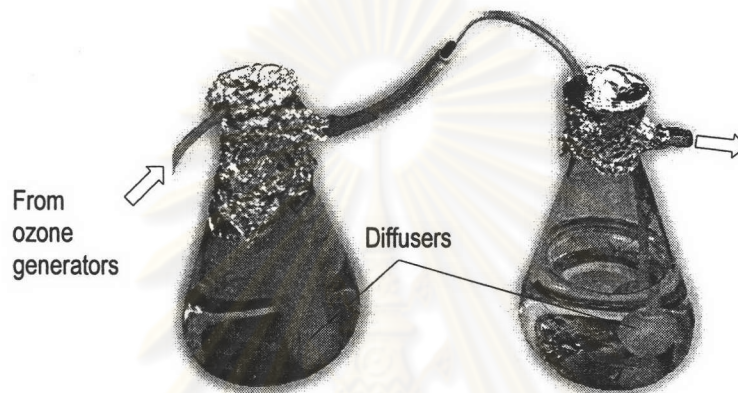
Figure 3.12 The assembly for a Standard Iodometry Method

By using these ozone generators, rates of ozone generation were approximately 4.2 mg/min and 23 mg/min when 2360 sccm air and 4720 sccm oxygen were used as feeding gases, respectively. According to these ozone generation rates and gas flow rates the concentration of ozone in feeding gas were 4.88 mg/l (6.12×10^{16} molecules /cm^3) and 1.78 mg/l (2.13×10^{16} molecules /cm^3), respectively.

3.3.1.4 Pulling Mechanism

Since pultrusion is the only common continuous composite manufacturing technique [21]. It is the most cost-effective of all methods for mass producing composite. The prototype UVO process was designed to apply in pultrusion. The mechanical pulling action was designed and utilized to engage the process. This unit functioned as fiber feeder to the UVO process. As the fibers were pulled from the fiber creel into the UVO reactor, the pulling speed must be able to adjust in order to examine the roles of exposure time.

Figure 3.13 illustrates the pulling mechanism of the process and its components. The pulling force was accomplished by a DC precision motor (b) which drives two rollers (a) to pull fibers from the creels. Pulling speeds were adjusted by varying DC voltage over the motor using an electronic circuit (d) and rotating knob (e). Roller surfaces were made from soft and smooth materials to prevent any effects and damage that may causes on the treated surface.

However, to evaluate the relationship between the adjusting knob (e) and linear pulling speed, a calibration curve is required after installed the pulling mechanism into the process. The rotating knob was scaled from zero to one hundred, which the minimum and maximum voltages were supplied the circuit respectively. Figure 3.14 illustrates a calibration curve of the pulling speed against the rotating scale.

In this study, the variation of exposure time was interested. The retention times of fibers in the UVO reactor for surface treatment are 2 min, 5 min and 10 min, which were corresponding to the linear speed at 0.5 m/min, 0.2 m/min and 0.1 m/min, respectively. Therefore to reach the speed of fiber pulling, the adjusting knob must be rotated to scale 44, 12 and 6, respectively.
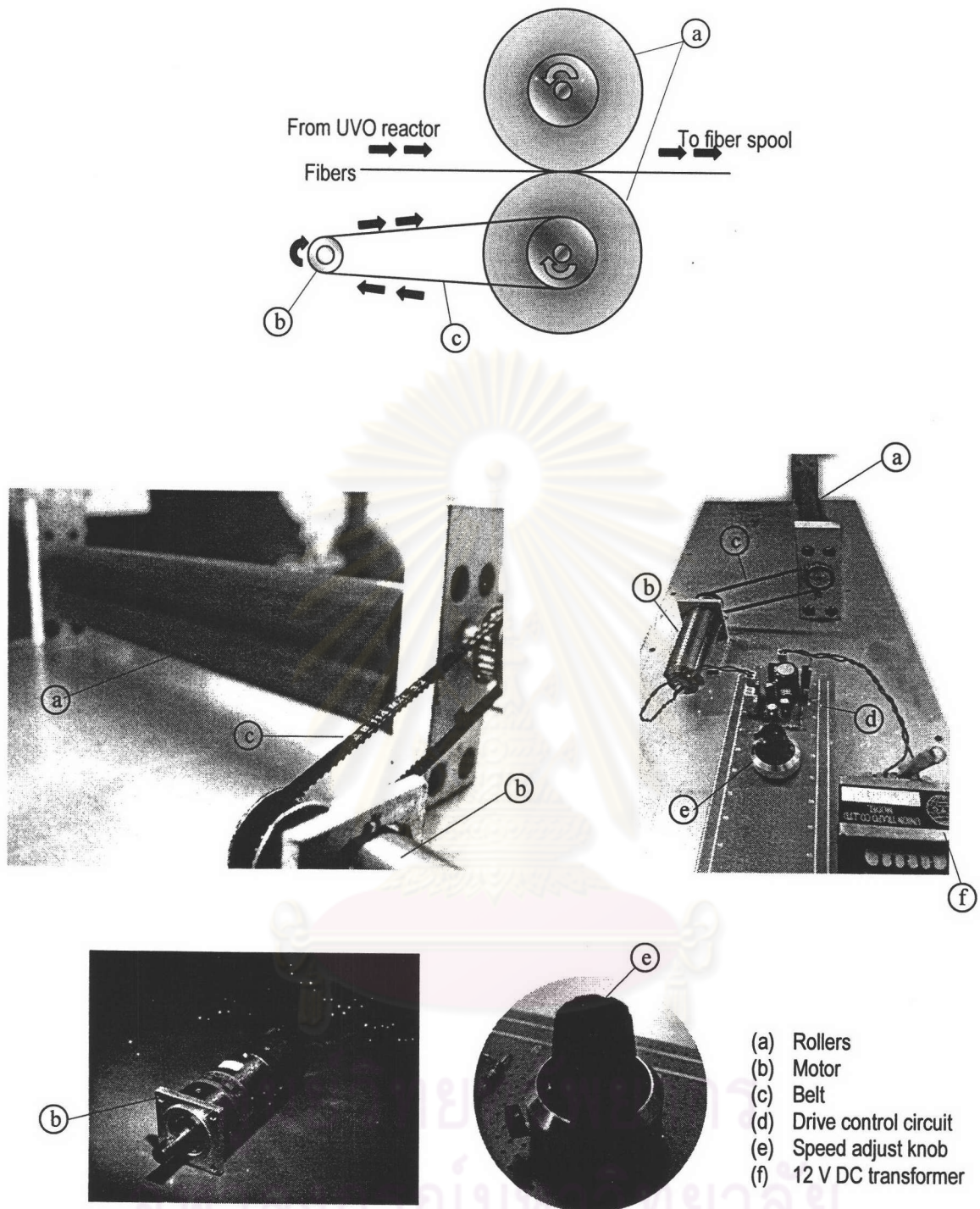
From UVO reactor

Fibers

To fiber spool

(a) Rollers
(b) Motor
(c) Belt
(d) Drive control circuit
(e) Speed adjust knob
(f) 12 V DC transformer

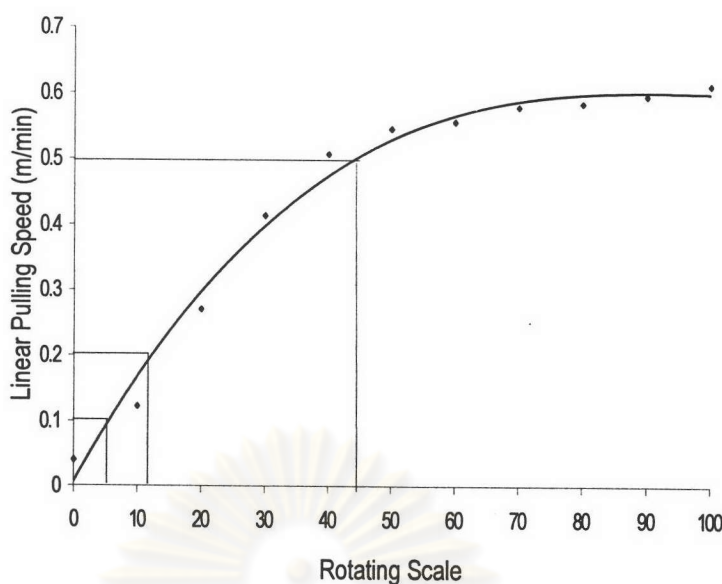**Figure 3.13** The pulling mechanism of UVO process.

Figure 3.14 The calibration curve of pulling speed against rotating scale on the adjusting knob.

3.3.1.5 Monitoring Devices

In this work, three parameters, pressure, temperature, and gas flow rate, were carefully monitored. All of these parameters were monitored to keep a constant reaction condition. Therefore the temperature measurement unit, pressure gauge, and rotameter (gas flow meter) were required to include in the system.

The temperature measurement unit was composed of three major parts: temperature sensor, transmitter circuit, and display. Temperature sensor is made of a semiconductor material as known as an electronic chip codename LM335. The sensor chip uses the principle that the electrical resistance of the semiconductor material changes with temperature. Voltage signal from the sensor was sent to the transmitter circuit where the voltage signal was calculated and converted into electrical current signal. The resulted current signal was sent to the seven-segments display that shown the temperature in digit.

The temperature sensor was mounted at the middle of the horizontal reactor chamber. The signal from sensor was sent through wires to the transmitter circuit which was installed in a plastic box. At the front side of the transmitter box a temperature display was mounted as well as the 9 volt DC supply connector and on/off switch.

The accuracy of the temperature measurement unit is ± 0.5 °C. However, after installation of the unit into the UVO system, a temperature calibration with a conventional thermometer was performed before any operation. Figure 3.15 illustrates a schematic diagram and some photographs of the temperature measurement unit.

To monitor pressure inside the reactor chamber, a spring pressure gauge was used. Its principle is that the pressure force is balanced by the movement of a spring. The position of spring can be related to the process pressure. In this system, the pressure gauge was mounted at the exhaust gas outlet. Another function of the pressure gauge is, for safety purpose, to prevent any increasing of pressure which may cause damage to the UV lamps inside the reactor chamber.

The last monitoring device was the rotameter. In this system, two rotameters were used to regulate the flow rates of the inlet gas, either N_2 or O_2, prior to entering into the reactor chamber. Flow rates of the gas can be adjusted by rotating knobs of the rotameters. These knobs functioned as needle valves to regulate the flows. Figure 3.16 and 3.17 illustrates some photographs of the pressure gauge and rotameters, respectively.
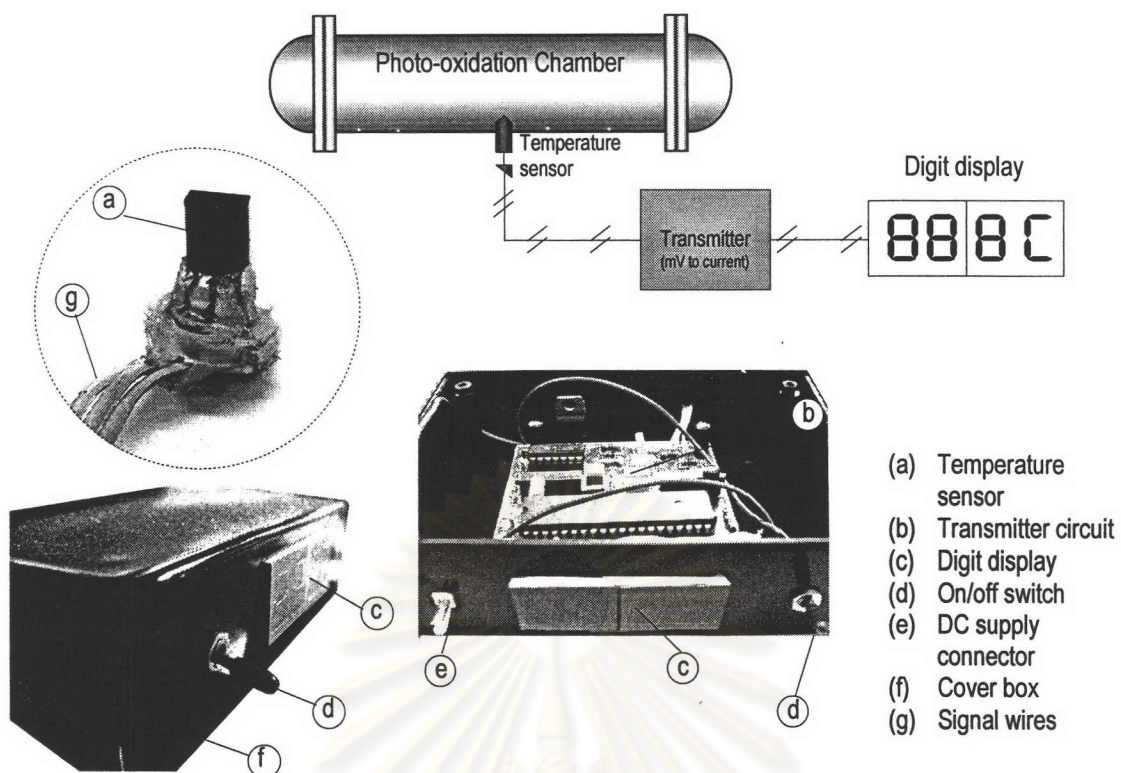
(a) Temperature sensor
(b) Transmitter circuit
(c) Digit display
(d) On/off switch
(e) DC supply connector
(f) Cover box
(g) Signal wires

Figure 3.15 Temperature measurement unit.

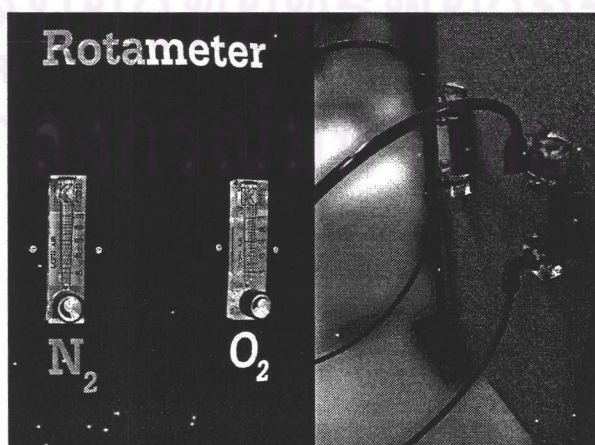**Figure 3.16** The pressure gauge.

Figure 3.17 Rotameters: front-view installation (left) and back-view connections to gas tanks (right).

3.3.1.6 Casting Mold

The mold designing was originated by an idea of simple but precise in dimensions. In this study, epoxy was used as the continuous phase, matrix, and polyester yarn as the discontinuous phase. Epoxy is thermoset polymer that can be cured in room temperature and special ambient is not necessary. Cold casting, the easiest and simplest method of polymer fabrication, was selected as the method for fabricating the test specimen.

Prior to designing the casting mold, it is necessary to select a method for testing. In this study, tensile properties of the composite were interested. Since the test specimen geometry should be simple and easy to fabricate, the ASTM D638M test method was used as a basis to fabricate composite specimens for tensile testing. Unidirectional and tensional arrangement of fiber in composite were additional criterions for designing mold, to achieve these goals the sample thickness should be high enough. The pictures-frame type mold was selected to design since it is suitable to use in laboratory, has no need of high production rate, and able to give "perfect" unidirectional tensile specimen. In this work, the thickness of specimens is 10 mm which is the maximum thickness allowed for this test method. Figure 3.18 illustrates the ASTM D638M type MI specimen and its dimensions used as basis of mold designing.
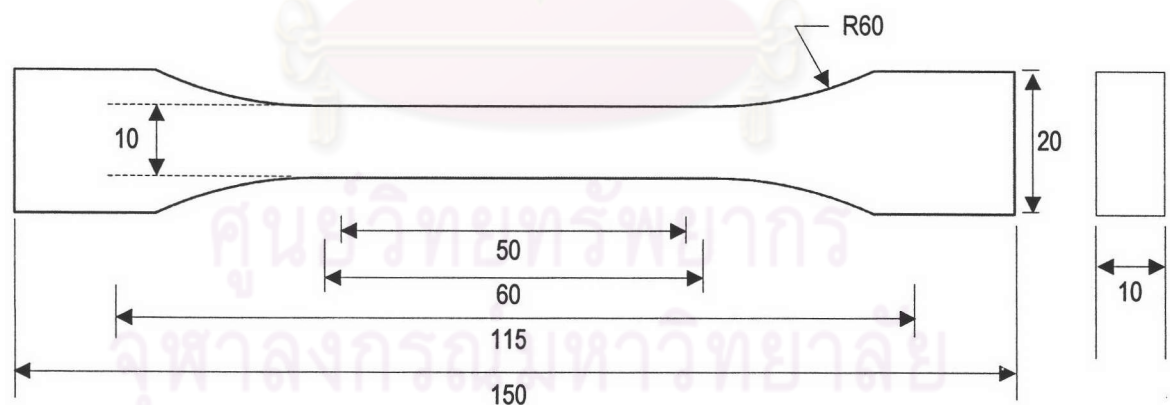

Figure 3.18 The dimensions of ASTM D638M type MI specimen for tensile testing (unit in millimeter).

The pictures-frame type mold was CAD-designed and 3D illustrated as shown in Figure 3.19. Nine pieces of "picture" were designed to assemble parallely to each other within the "frame", the space between two adjacent pictures is 10 mm which is equivalent to the narrow section of the test specimen in Figure 3.18. Together with pictures and frame, this mold gives eight cavities for filling the mixture of resin and hardener. At each cavity, both sides of the "frame" were designed to have an array of sixteen drilling holds within the narrow section of the specimen, 10 mm × 10 mm, for aligning of yarns. The diameter of drilling holds was designed to 1 mm, these small holds were designed to prevent large amount of resin leakage.

Stainless steel type 304 was selected as a material for making of the casting mold. The pictures were shaping by machining with extremely accurate in dimensions. The rectangular frame was made by machining each side to the specified dimension; the two longer sides were drilled to have eight arrays of yarn aligning holds at the position respect to the narrow section of the specimen, all four sides of frame were welded together to get the frame as designed. Figure 3.20 shows some photographs of the pictures-frame mold and assemble method for resin casting of the testing specimen. This fabricating technique resulted a composite specimen contained approximately 10 % by volume of PET fiber.
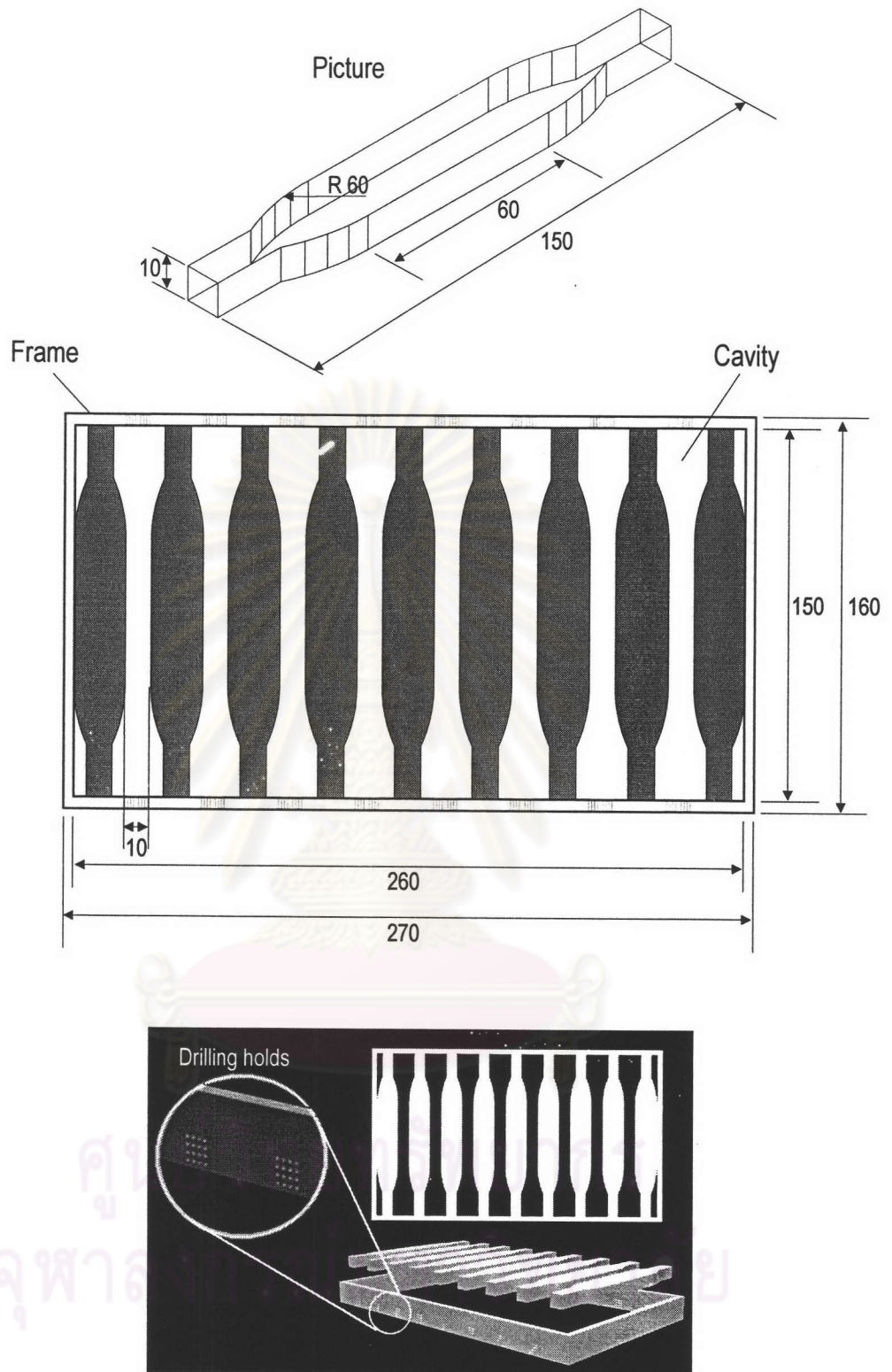
Picture

R 60

60

150

10

Frame

Cavity

150

160

10

260

270

Drilling holds

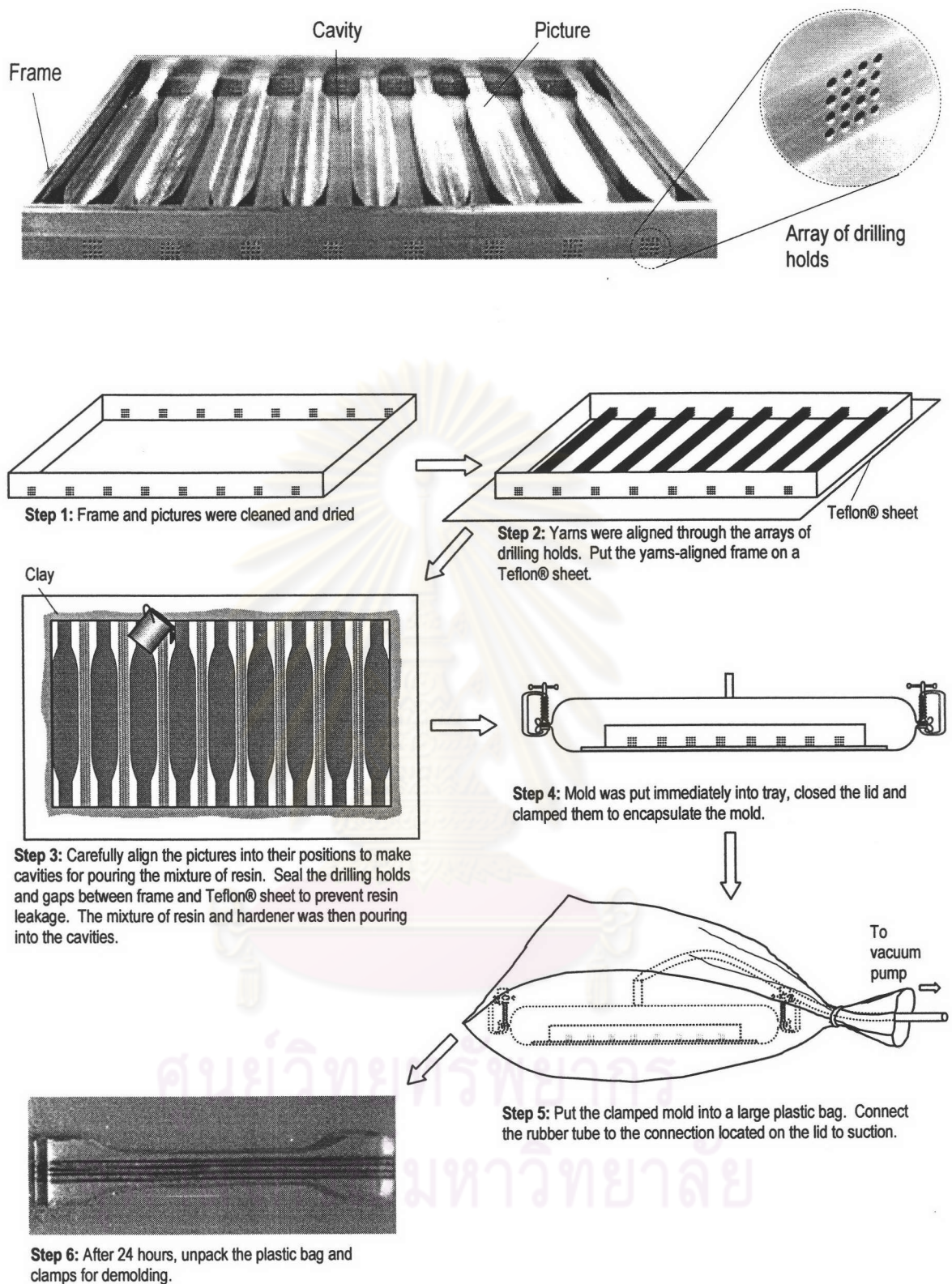**Figure 3.19** CAD-designed and 3D illustrated of the pictures-frame casting mold

Figure 3.20 Photographs of the pictures-frame mold and assemble method for resin casting of the testing specimen.

3.3.2 Process Construction

After all equipments (UV light sources, reactor chamber, ozone generators, pulling mechanism, and monitoring devices) were constructed, the next step is connecting and arrangements of the equipments to start an operation. The process layout mentioned in section 3.2 was helpful in this step. Some equipments, however, were arranged differed from the layout.

Tubing and electrical wiring were main tasks in this step. Two different types of tube, polypropylene (PP) and polyurethane (PU), were used for tubing. The first tubing was used for flexible-required locations in the process such as at the connections between the ozone generator and the reactor chamber. The latter tubing was used at the high pressure connections, e.g. from gases supply tanks to rotameters and from the rotameter to flow junction. The flow pattern of gases in the process is shown in Figure 3.21 where solid lines and dotted lines represented PP and PU tubing, respectively.
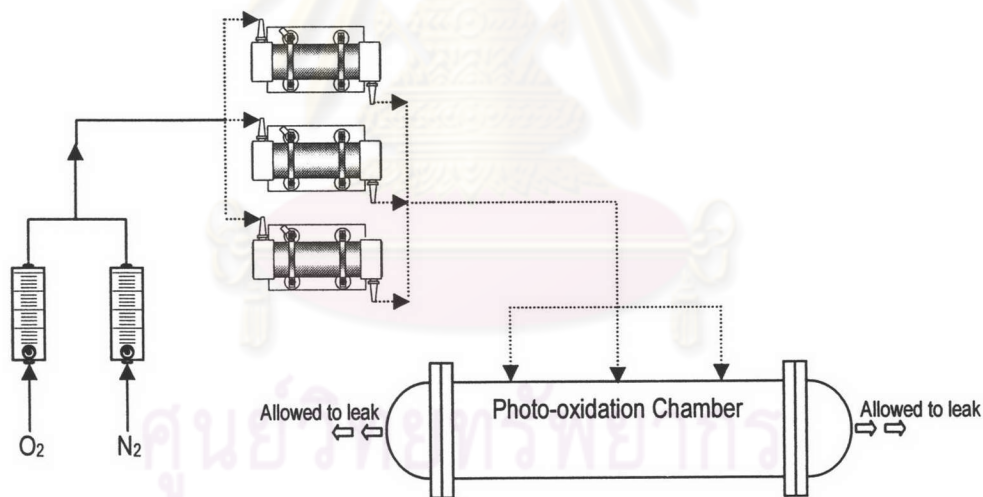

Figure 3.21 Flow diagram of supplied gases

For wiring, there are four equipments needed for electric supply; UV light lamps and their control unit, ozone generators, pulling mechanism, and temperature measurement unit. Insulated wires, junction, and connection were used in this entire process. In case of wiring inside the reactor chamber, wires was covered with aluminum tape to protect any effects of reactive species as well as UV light in the reactor which can cause uncertain condition.

Introducing of yarn and setting up of pulling mechanism were the next steps after tubing and wiring. Resulting from preliminary test, number of yarns to be pulled in each run was twenty four yarns, which gave a surface modification rate of the process as 12, 4.8, and 2.4 m/min corresponding to the retention time of yarns in reactor of 2, 5 and 10 min, respectively. The yarn creels were installed into rack as illustrated in Figure 3.22. All twenty four yarns were grouped and pulled into the reactor chamber, through a small hold, by the pulling mechanism located another side of the reactor chamber. At the exit of reactor chamber the group of yarns was split into four groups to comfort the fabrication of tensile specimen. Yarns were then collected into fiber spools.
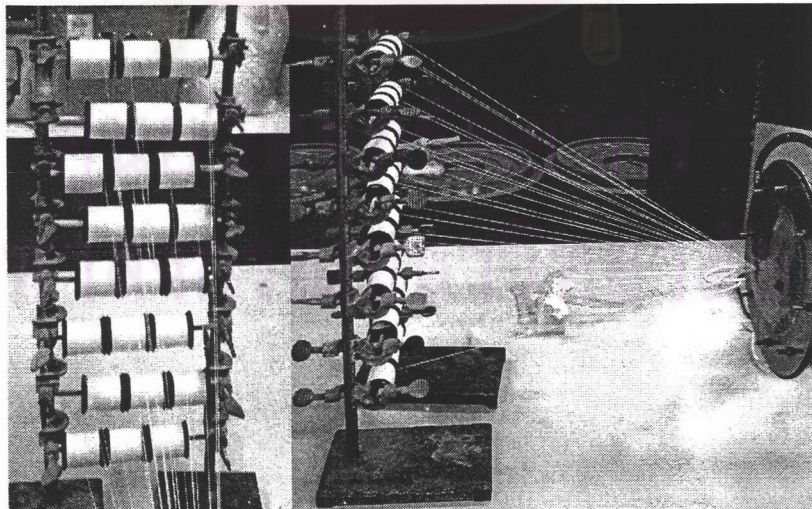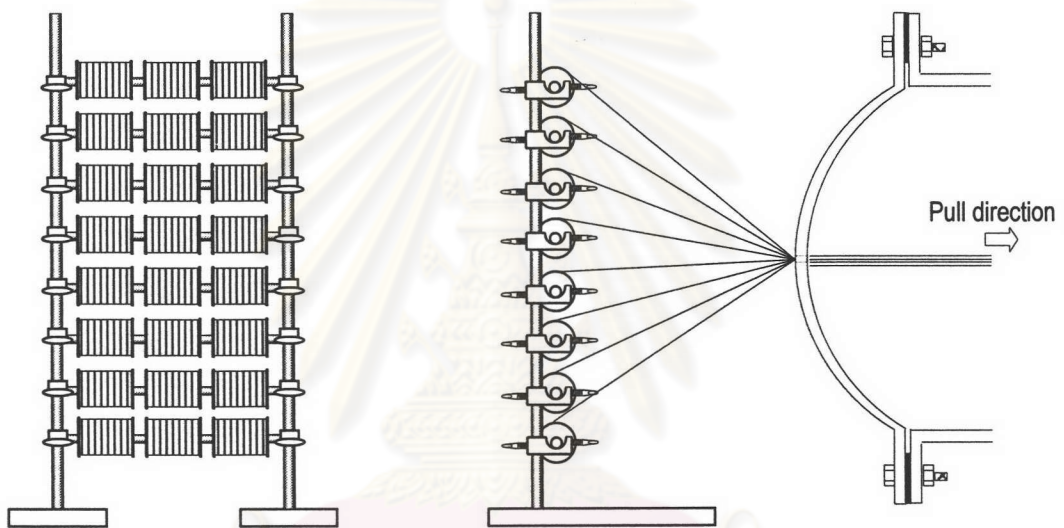

Figure 3.22 Drawing of the rack of yarn creels (up left), and schematic of introducing of yarns into reactor (up right). Photographs of constructed fiber creels rack (bottom).

Next and last step before starting the experiment was to evaluate the starting conditions of the process. There are two conditions that have to ensure that they were reached the equilibrium state, temperature and gas species. In another words, this step is to find an optimum time before introducing yarns into the reactor for modifying their surfaces.

Temperature inside the reactor chamber was influenced by the heat generated by UV lamps, gas feeding flow rate, and surrounding temperature. Since the flow rate of gas species was fixed at the same rate all over the experiment regimes (10 scfh) as well as the gas feeding temperature which was assumed to be constant at room temperature (~ 37 °C). Heat produced due to the UV lamps seemed to be the only factor affecting the temperature inside the chamber. To find time interval to reach the constant temperature, changing of temperature inside reactor chamber was recorded after UV lamps were switched on. Figure 3.23 shows the plot of temperature inside the chamber against time after the lamps switched on.
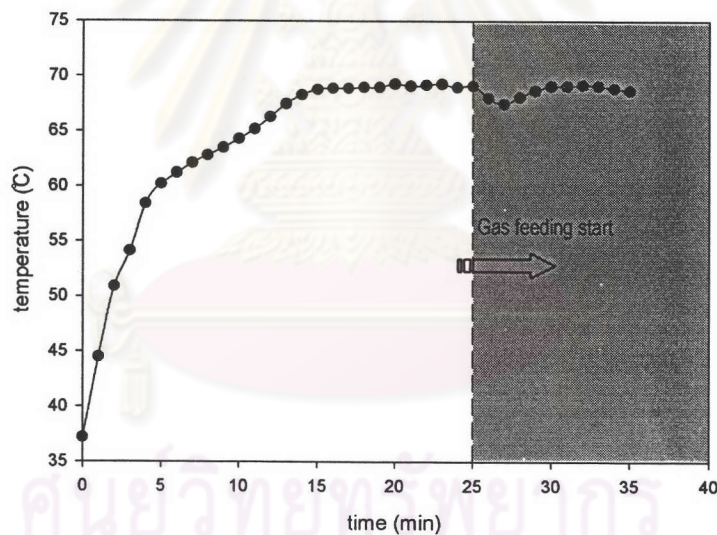

Figure 3.23 The interior temperature after lamps was turned on.

From Figure 3.23, the inside temperature reached constant value (~70 °C) after approximately 17 mins. About 1-2 °C decrease of the inside temperature was observed after feeding gas species. The temperature, however, was recovered to the constant temperature again within 7-8 min.

The equilibrium state of gas species was reached after feeding was started more than 1 min (this value was calculated by assumption base on gas species were behaved as incompressible fluid). This can be concluded that time to reach an equilibrium state is about 25 min. In practice, the experiment should run after this period of time to ensure that the steady state of the continuous process was performed. At this point the process was ready for running the experiment. Figure 3.24 is shown the constructed process and its components.
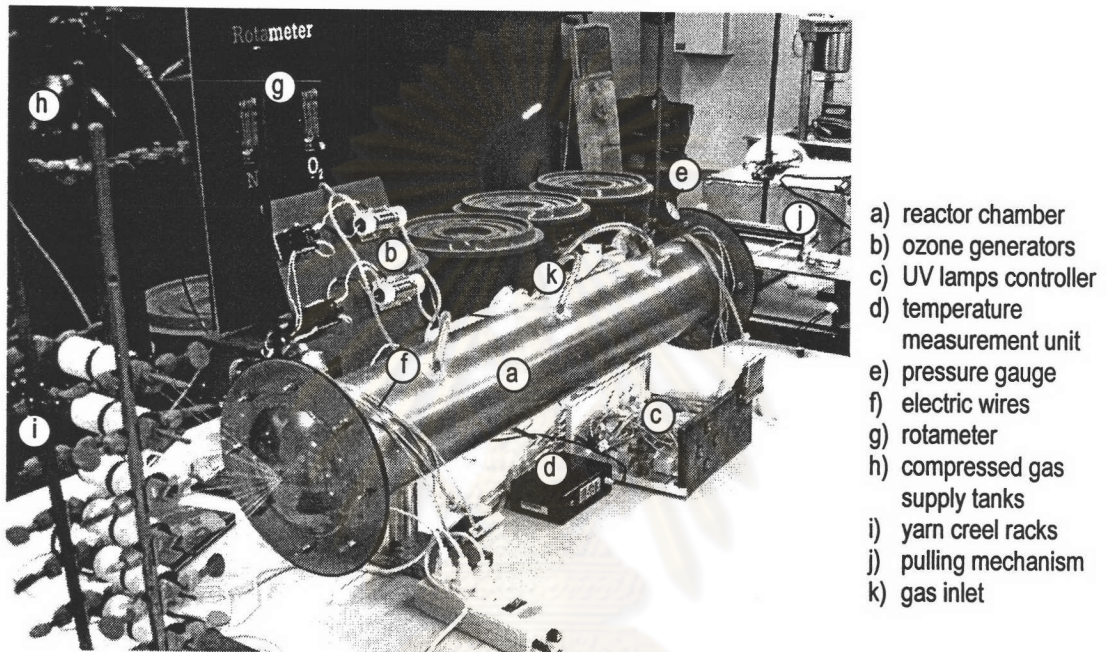

a) reactor chamber
b) ozone generators
c) UV lamps controller
d) temperature measurement unit
e) pressure gauge
f) electric wires
g) rotameter
h) compressed gas supply tanks
i) yarn creel racks
j) pulling mechanism
k) gas inlet

Figure 3.24 Constructed process and its components.

3.4 Characterization and Testing

3.4.1 PET Fiber

The surface-treated PET fiber samples were analyzed by SEM/EDX and tensile testing. SEM micrographs of fiber surface morphologies were obtained on JEOL JSM-5800 LV. The microscope operated at 15 kV accelerating voltage. Prior to SEM observations, all samples were sputter coated with gold.

EDX spectra were taken in an OXFORD ISIS 300 x-ray energy dispersive analysis system, which was attached to the microscope. In this study EDX study was used as preliminarily examine the oxygen contents on the near-surface region of the samples. EDX samples were attached on carbon stubs. The EDX was performed without coating of the yarn samples. Oxygen content results were taken as the average values from three different positions on a fiber surface.

The tensile properties of PET yarns were determined by means of a LLOYD 500 according to ASTM D3379-75. The testing was performed at room temperature. All samples were equipped with a 100 N load cell. The tensile strain rate was 20 mm/min. All the results were taken as the average values of 5 samples.

3.4.2 Composite Specimen

Tensile tests of the composite specimens were carried out on a universal testing machine Model LLOYD 500 equipped with a 10 kN load cell, according to ASTM D638M-91a. The cross-head speed used for the type MI tensile specimens was 5 mm/min. For the tensile tests the stress-strain data were exported via the NEXYGEN software (bundled with the testing machine). The ultimate tensile strength, strain at break, and toughness of the composite specimens were calculated by using MATLAB version 5.3.1. The toughness of the materials was estimated using trapezoidal numerical integration. All the results were taken as the average values of 5 samples.

The surfaces of the fractured PET-fiber/epoxy composites specimens under tensile tests were examined using a scanning SEM JEOL-58000LV. Prior to SEM observations, all samples were sputter coated with gold.