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IMPROVING THE TEMPERATURE MEASUREMENT IN HYDRO-PROCESSING REACTORS

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ABSTRACT

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The world is going to replace renewable and green fuels with fossil fuels to reduce the environmental issues and global warming effects. Bio-based feedstock is a biological source to produce fuel and considered as an alternative that can supersede fossil-based resources in the future. Co-processing is a transition towards green fuel which through a mixture of fossil and bio-based feedstocks are processed.

In co-processing, the biomass is blended with fossil-based feed and upgraded through hydro-treating in a catalytic reactor. Since biomass contains high amount of oxygen, the process is highly exothermic releasing heat and causing temperature rise inside the reactor. Hence, reactor temperature needs to be monitored properly to prevent serious accident and retain the required quality of the product. In petro-refineries, use of temperature measurement systems is a need and usually problematic in hydro-processing reactors. When introducing alternative or biomass feedstocks to the process, the problem will be more highlighted due to new reactants and different reactions.

The following work has expounded the need for measuring temperature in exothermic reactions. Reactions and products, main hardware and equipment has been described to express the need for temperature monitoring systems.

This thesis has considered different approaches and methods in measuring the temperature in reactors mentioning their advantages and disadvantages. Challenges stemmed from the new reactants and new reactions by introducing bio-based feedstocks were identified.

The material selection is crucial as almost all available temperature measurement systems has direct contact with the reactants and catalyst. Some widely-used materials in oil and gas industry were compared to choose the proper one for the application. The possible solutions reducing the problematic issues were recommended for design, procurement and installation of the temperature measurement system.

Keywords: oil and gas, bio feedstock, biofuel, co-processing, hydro-processing, hydro-treating reactor, multipoint temperature measurement, MI cable, thermo-element, sheath material

PREFACE

This master thesis is the completion of Master education in Electronics Engineering.

The basis of this study was research and study of different types of temperature measurement systems applying in hydro-processing catalytic reactors and challenges related to multipoint temperature measurement systems.

This master thesis study was funded by Neste Engineering Solutions Oy, Porvoo, Finland. During this research, the author has been working in this company.

I would like to thank my university supervisor, Professor Lauri Sydänheimo, and the company supervisor, Otto Rossi, who shared their knowledge, information and constructive comments to the thesis.

I would like to recognize the assistance I received from my colleagues and friends, they provided me with invaluable experiences and sincere help.

I have to thank my wonderful parents and family for always supporting and loving me throughout my life. In particular, very warm thanks go to Mehdi Bahiraei, my dearest brother for his encouragement and helpful advice during this research and my academic life.

Tampere University, 7.2019

Leila Bahiraei

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LIST OF SYMBOLS AND ABBREVIATIONS

ASS	Austenitic stainless steel
CI-SCC	Chloride Induced Stress Corrosion Cracking
Cl	Chloride
CTO	Crude Tall Oil
CO	Carbon Monoxide
CO_2	Carbon Dioxide
EAC	Environmentally Assisted Cracking
FBG	Fiber Bragg Grating
FCC	Fluid Catalytic Cracking
HE	Hydrogen Embrittlement
HCl	Hydrogen chloride
HDM	Hydrodemetallation
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulphurization
H_2S	Hydrogen Sulfide
IR	Infrared
m	meter
MI	Mineral Insulated
mm	millimeter
MgO	Magnesium Oxide
RTD	Radial Temperature Difference
NDT	Non-destructive testing
NH_3	Ammonia
Ni	Nickel
NOx	Nitrogen Oxides
SCC	Stress Corrosion Cracking
SOx	Sulphur Oxides
ΔT	Temperature rise

1. INTRODUCTION

Fossil fuels are gradually replaced with renewable and alternative fuels produced from biomass, wood, waste, or other biological sources. The use of renewable fuels is growing steadily worldwide to reduce greenhouse gases and CO_2 emissions, combat climate change and supply the rising society´s demand for energy.

Biomass including non-edible oils, tall oil[1], pyrolysis oil, waste vegetable oil, animal fat, forestry, and paper waste is considered as an alternative feedstock for fuel production. Biodiesel and renewable diesel can be produced by processing this feedstock and expected to replace petro-diesel fuel in the future.

Several conversion routes to converting biomass and renewable feedstocks to liquid transportation bio-fuel have been developed. The conversion can occur where fossil fuel and renewable feedstock are blended and co-processed producing a clean and green diesel. Another conversion route is through new process and dedicated stand-alone units in which renewable feedstock is processed to produce 100% renewable fuel. Co-processing is an attractive option for refiners, since the petro-refinery infrastructure and processes would be used for processing of bio-blended feed and producing renewable fuel with no additional intensive investment. [1, 2]

Catalytic hydro-processing and fluid catalytic cracking (FCC) are two main technologies used for the co-processing of bio-feedstocks in standard refineries. Before co-processing, hydro-treating process upgrades the biomass feed to be used in FCC co-processing [3, 4]. Hydro-processing is a crucial and vital process in either co-processing or petro-diesel production [1]. The process is to remove impurities and poisonous contents or components and to produce lighter hydrocarbons through chemical reactions and hydro-treating. The occurrence of reactions is in the presence of hydrogen and hydro-treating catalyst inside a reactor. The amount of hydrogen injection depends on the type and amount of bio feedstock added to fossil fuel in co-processing route [1]. Although this process is called hydro-treating in both bio-based fuel and fossil-based fuel productions, different impurities and pollutants with different weight percent values are removed in these fuel production processes. It means different reactions happen in these two processes.

In petro-diesel production, the reactors are the core equipment in hydro-treating process. In order to control the reactor condition and reactions, reactor temperature is usually monitored. The reactor temperature has direct impact on the quality and quantity of the product. For the early detection of critical operation state, safety, saving valuable maintenance

[1] Tall oil is the byproduct of Kraft-pulping process and “Tall” refers to pine tree in Swedish [5].

time and reducing maintenance intervals, temperature monitoring of reactors is essential. Hydro-treating reaction temperature needs to be monitored precisely to avoid reactor run-away, catastrophic accident and to keep the required quality of the product.

Reactor temperature measurement is challenging issue in refineries and when introducing new feedstock into the process seems to be even more problematic. Due to high amount of oxygen content in bio-based feedstock, the reactions inside reactors are highly exo-thermic [1, 3, 4, 5, 6]. Temperature rise has to be detected at the very early stage and need to be controlled properly.

The purpose of this thesis was study and research different types of temperature measure-ment systems usable in reactors and vessels to identify the advantages and drawbacks of each type. The reactions, reactants and byproducts in co-processing and bio-fuel produc-tions were studied to find out the potential challenges and possible solutions specifically material selection addressing the issues.

One of the widely-used type of hydro-processing reactors; a trickle bed reactor was de-scribed in order to give an overview of reactor structure and its operation to readers, oth-erwise it depends on the process type, design and application to select the proper type of reactor.

In this research, the importance of equipping reactors with temperature measurement sys-tems when occurring exothermic reactions was studied. Using the available scientific lit-eratures, and handbooks about the reactions in bio-derived fuel production, potential and extra challenges of temperature measurement systems were identified. How to select tem-perature measurement type and thermo-element sheath material and how to install the assembly with less issues were detailed providing the results of the thesis.

2. HYDRO-PROCESSING REACTOR

In petroleum refineries, hydro-processing is the process of adding hydrogen to petroleum entailing two separate but similar processes; hydro-cracking and hydro-treating. Hydro-cracking reaction occurs in higher pressure and uses more catalyst than hydro-treating reaction and breaks the carbon-carbon bonds. Hydro-treating is the removal process of undesired chemicals like heteroatoms, halides, sulfur, nitrogen, oxygen, and organometallic compounds besides producing light hydrocarbons. Both reactions uses catalysts, but the amount and the type of catalyst are different. [7]

Process conditions for hydro-treating and hydro-cracking processes are shown in Figure 2.1.

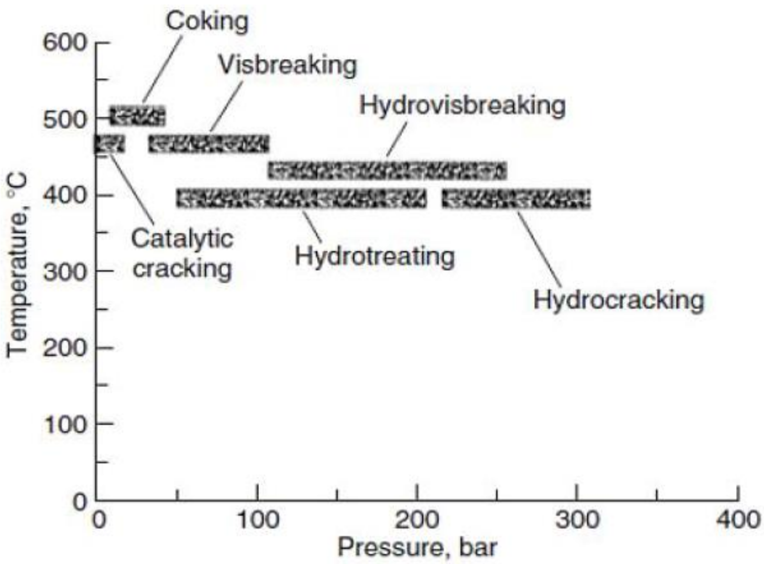

Figure 2.1: Pressure and temperature ranges for refinery processes [8]

Studies show renewable and bio-fuel can be produced from bio-based feedstocks under specific condition [1, 6] which is called stand-alone conversion route or via co-processing of fossil fuel and upgraded bio-feedstock. A common method in producing bio-fuel in any of above mentioned conversion routes is catalytic hydro-treating in which inlet feeds react with hydrogen in the presence of metal catalysts in a reactor [1, 3, 6, 9]. This reaction occurs in proper ranges of temperature and pressure 250°C - 400°C and 10-18MPa, respectively [6].

The removal of harmful and poisonous chemicals, as the main purpose of hydro-treating, is very important. It prevents poisoning the reactions of other refining processes. Depending on which component to be removed; hydro-treating reaction is called hydrodesulphurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodemetallation (HDM) for removing sulfur, nitrogen, oxygen, and metallic compounds, respectively. These reactions occur during hydro-treating. [7]

Depending on the type and amount of bio-derived or renewable feed introduced to the process, new reactions and new products occur which need to be taken into account. Injection of new bio-based feedstock into hydro-treating process forms high amounts of propane, water, carbon monoxide (CO), carbon dioxide (CO_2), and methane [1]. Additionally, H_2S and NH_3 are formed due to HDS and HDN reactions in the process [6]. Renewable feedstock stemming from vegetable oil and animal fat contains triglycerides, fatty acids, and impurities like alkalis and phosphorus [6]. Hydrogen consumption depends on the feedstock type. Due to very low amount of sulfur and nitrogen in bio-based feedstock, HDS and HDN reactions are very low [1]. Furthermore, bio-based feedstock due to acidotic contents [1, 5, 6] makes a corrosive hydrothermal environment. For instance, tall oil contains free fatty acid and resin acid [1, 5] which increases corrosion negatively. The equipment and hardware are subjected to corrosion causing necessary changes in material selection.

In conventional hydro-processing to convert crude oil to fuels with high quality, since the amount of oxygen is less than 0.3 wt%, more focus is on removing sulfur and nitrogen than oxygen. Feedstock derived from bio-organic and fat rich materials contains new types of molecules with a high oxygen content. This amount of oxygen depends on the feedstock type and may approach 50 wt% which needs to be removed by hydro-treating process. Since this high level of oxygen is treated, the characterization of hydro-treating is mostly hydrodeoxygenization (HDO). [6]

Formation of water, CO and CO_2 removes oxygen in reactors through dehydration, decarbonylation, and decarboxylation reaction routes. These three different routes of oxygen removal are shown in Figure 2.2. The catalyst type, feedstock type, the amount of injected co-processing feedstock, reaction condition, and hydrogen content control the HDO routes. [3, 6]

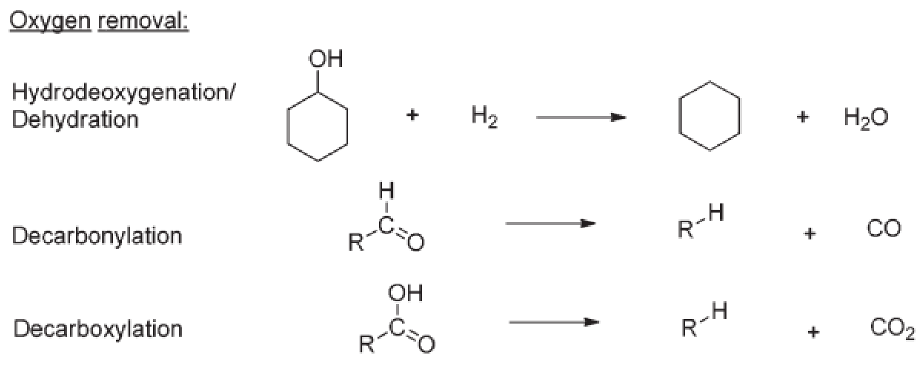

Figure 2.2: Oxygen removal reactions in hydrodeoxygenation routes [3].

The selection of reactor type depends on process condition and engineering aspects. Among the hydro-treating reactors, trickle-bed type is widely applied in hydro-treating process due to its simplicity and flexibility [10]. Reactors are the core equipment in this process. The reactor has to be multiphase due to three-phase process (solid, liquid and gas) inside the reactor [9]. Most hydro-treating units are trickle-bed reactors in which the liquid and gaseous reactants flow down the solid catalyst loaded on fixed-beds [7]. Figure 2.3 illustrates a section of reactor beds with the quench zone.

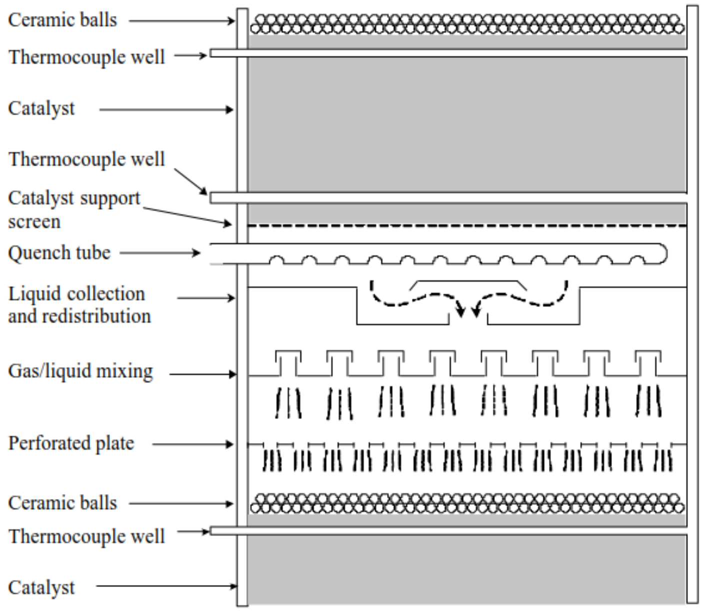

Figure 2.3: Hydroprocessing reactor, quench zone between the reactor beds [7].

Trickle bed reactor is a tubular tank sometimes very high about 10-30 m [11] including catalyst fixed-beds with quench zones in between, gas inlet, gas outlet, process liquid inlet, and outlet. The number of catalyst beds and quench zones and location of inlet outlets depend on the design condition. Maximum utilization of catalyst, desired mass velocity, acceptable pressure drop, heat release and reactor temperature affect the design of reactor; size, dimension, and bed numbers. [12]

Feed distribution, feed quality, and quench zone design have direct effects on the efficiency of trickle bed reactor [13]. Some hydro-treating process variables are reactor temperature, feed quality and rate, hydrogen partial pressure, hydrogen to oil (H_2/oil) ratio, and catalyst contaminants. Feed rate and product quality are two parameters clarifying the required temperature inside the reactor [12].

Hydro-treating reaction in bio-fuel production is strongly exothermic [1] which needs to be controlled and monitored properly. An exothermic chemical reaction in reactor has the potential to cause a thermal runaway which is the most critical safety limit for the reactors [14].

When the generated reaction heat exceeds the removed heat, this excess heat increases the rate of reaction and heat generation exponentially. Over pressurization and mechanical destruction of the reactor can happen due to high amount of released energy and rapid gas generation. Thermal runaway needs to be prevented to protect the catalyst and controllability of the reaction. [15]

The formation of hotspots is one of the main problems of trickle bed reactors. Hot spots may form due to non-uniform distribution of gas and liquid flow inside the reactor. Hotspot is referred to a local maximum temperature inside the reactor. It has the potential to affect the yield of the products, deactivate the catalyst and it may lead to a thermal runaway when it happens near the reactor wall. When liquid is trapped in a blockage and cannot convect in the radial and axial direction, local hotspot is formed. Local mal-distribution is one of the possible mechanisms causing hot spots in trickle bed reactors. [16]

Channeling or wall effect, is high local velocity of flow in the bulk of the bed or near the reactor wall. Wall effect is not considerable in commercial trickle bed reactors. This phenomenon is usually observed in laboratory and pilot-scale trickle bed reactors due to the smaller ratio of the reactor to the particle diameter compared with the commercial reactors. When the liquid or gas flows downward, the liquid tends to move towards the wall and bypass the catalyst by choosing the lower resistant channels. [16] Non-uniformity in the catalyst bed properties results in bed channeling which leads to heterogeneity of catalyst wetting at the reactor scale. Incomplete wetting of catalyst particles by liquid decreases the catalyst utilization and reactor efficiency. Larger incomplete wetting areas inside the reactor can also form the hot spots. [11, 16]

Maximum temperature rise in reactors is one of the important factors in reactor design. Depending on process condition, the allowed temperature difference is between 15 ˚C and 30 ˚C [10]. Usually when the maximum allowable ΔT (temperature rise) inside the reactor is up to 42˚C, a single bed reactor can be applied and reactor temperature can be controlled by changing the reactor inlet temperature. For ΔT more than 42˚C, a multi-bed reactor with quench zones is designed to improve the fluid redistribution and release the heat which maintains ΔT within an acceptable and design limit. The gaseous hydrogen is injected to the reactor through quench zones to control the temperature. [12]

In ideal and uniform flow distribution in a reactor bed, the temperatures of all points at the same level are equal. The hottest part is the nearest level to the quench and the coolest part is the highest level of the bed. Since in real reactor beds, the flow distribution is not uniform, the temperatures of points located at the same level are not equal and the temperature difference is more at the bottom of the bed. The difference between the highest and lowest temperature at the lowest level of reactor bed is called "radial temperature difference" (RTD). Measuring the actual maximum and minimum temperature is almost impossible by available technologies, there is no measurement system to monitor every points. If the measured RTD was less than 3 ˚C, the flow distribution is assumed uniform but if larger, there is a potential reason stemming from blockages, hot spots, etc. [7]

Figure 2.4 shows a trickle-bed reactor with three beds and two inter-bed quenches. Maximum allowable temperature limits the length or depth of the reactor bed. Dividing total volume of the reactor into several beds limits the volume of the reactor to smaller and safer portions. The temperature profile shows that heat release rate is decreased from top to down of the reactor, therefore it is typical to design the reactor with deeper beds at the bottom. [10]

When loading the new catalyst, the lowest possible temperature is set and increased by the time to compensate the activeness of the catalyst. Over the time, activity of the catalyst is gradually decreased. In order to maintain the output product with the same quality; reactor bed temperature has to be increased usually by less than 1˚C per month. This increase is possible by raising feedstock temperature. The temperature increase continues up to a certain mark close to the maximum design bed temperature or ending the catalyst life. The catalyst life is estimated by the quality of the output product and required feed temperature. [12]

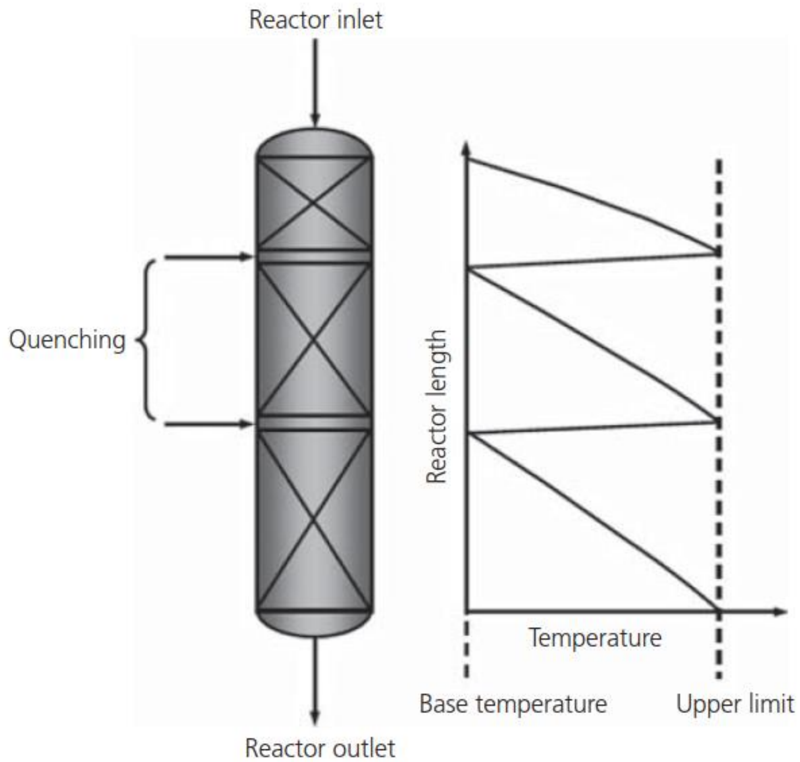

Figure 2.4: Hydro-treating reactor with inter-bed quenches [10].

When increasing the reactor temperature, some unwanted or side reactions will happen or the rate of reactions will increase and control of the reactor will be more difficult [16].

Higher reactor temperature results in higher sulfur and nitrogen removal and quicker coke formation. The latter is not desirable as it reduces the product quality and catalyst lifetime. Coke formation causes catalyst deactivation leading to earlier catalyst change and increasing operation cost. [8]

When setting the reactor temperature limits, it needs to be monitored and controlled continuously to maintain the product quality, predict the catalyst life, detect the hot spots and prevent the reactor runaway. Prediction of catalyst life can reduce the maintenance cost since the number of unexpected shut down is decreased and pre-planning the shut down time will be possible.

3. TEMPERATURE MEASUREMENT METHODS IN REACTORS AND VESSELS

Depending on industry and application, different methods and technologies are applied to measure the temperature. Additionally, process conditions, reactions, hazardous media, vibration, corrosion rates, design and operational pressure, and temperature values influence the selection of temperature measurement type.

In catalytic processing units and reactors applying in petrochemical, oil and gas industry, different internal and external variables impact reactions, catalyst bed temperature and catalyst lifetime. Hot spots, poor sealing, channeling, and non-uniform flow distribution are undesirable process phenomena which need to be monitored. Monitoring and on-time detecting of them will increase the performance, catalyst lifetime and product quality. Temperature measurement can be considered as an approach to monitor these phenomena.

Proper temperature profiling will extend ability to indicate hot spots, predict the catalyst lifetime, enhance the safety, decrease the maintenance cost, increase the production, and improve the product quality. Different generations and methods of temperature measurement have evolved from traditional thermometers for this purpose. For monitoring the temperature, specialized instruments like multipoint thermometers, skin-point thermometers, and imaging systems are used in reactors and process vessels. Different sensor types such as thermocouples, resistance temperature detectors and infrared sensors are utilized to sense the temperature. Fiber optic technology and optical sensors introduced to the market are also applied for temperature measurement.

To a great extent, temperature measurement systems made by different manufactures are similar. Pipe-well (rigid) multipoint and flexible-radial multipoint are two methods of temperature measurement systems which are widely used to measure the temperature inside the catalytic reactors. Surface or skin temperature measurement is an additional measurement system monitoring the body temperature of vessels, hydro-processing reactors, tanks, and other exothermic applications. It depends on the process, reactions and application to choose if internal multipoint temperature measurement or external surface temperature measurement or a combination of both systems need to be utilized for temperature monitoring of vessels or reactors.

A flexible radial multipoint temperature measurement system is more complex than the pipe-well type. This technology is also applied in nuclear industry to measure the temperature inside the nuclear reactors in power plants. Temperature inside the nuclear reactor is around or beyond 1000°C while the reactors in refineries operate in lower temperatures. In addition, reactions and reactants differ in reactors operating in different industries. Therefore, criteria for selection of sensors and materials are based on the reactor application and operating condition. While a material like Inconel 600 and 690 [17] is an appropriate choice for the sheath of thermo-well installed in a nuclear power plant reactor, it may not be a suitable material for thermo-wells in hydro-processing reactors. Reaction features, temperature and corrosive level of reactor environment in nuclear and oil and gas industry are decisive factors in material and sensor selection.

The manufacturers like Thermoelectra, Gayesco/Wika, Endress+Hauser, Rodax, Siemens and Daily Thermetrics have introduced their multipoint measurement systems to the market. These systems are described in the following sections.

3.1 Traditional temperature measurement system

A traditional temperature measurement system is an assembly of a single thermo-sensor inside of a rigid protective thermo-well.

The most common thermocouple is manufactured with a metal sheath mineral insulated cable. The metal sheath is filled in with compacted Magnesium oxide (MgO) powder and tip of the cable is temperature sensing area (Figure 3.1). Thermocouples are designed to withstand the operating pressure, temperature and vibration.

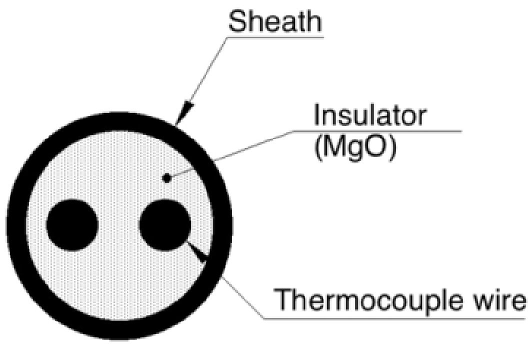

Figure 3.1: Section of thermocouple MI cable sheath [18].

Based on the design temperature of the reactor or vessel, thermocouple type (N, K, J, E…) can be selected. Connection head type of the thermocouples is either ungrounded (isolated from the sheath) or grounded (bonded to the sheath) as shown in Figure 3.2. These thermocouples can also be used without protective tubes (thermo-well), if the sheath is selected properly to be used in the required environment.

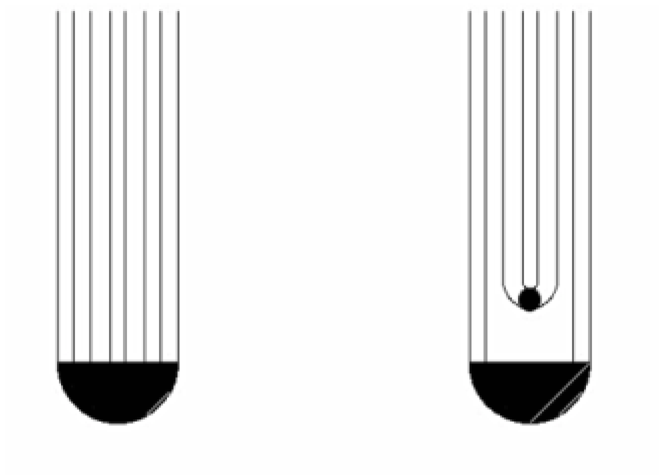

Figure 3.2: Connection head type of thermocouples [18].

In case of using the traditional method, MI cable inside the thermo-well, to measure the reactor bed temperature, the thermo-well has contact points with the catalyst. Since every thermo-well includes only one element, only one point inside the reactor can be monitored through one thermo-well. This method is not a practical and useful method in monitoring the reactor temperature. Adding any new measuring point means a new thermo-well which needs a new nozzle or tapped thermo-well on the reactor shell resulting in poor sealing. In addition to sealing issues, every additional bar, support, lever or even thermo-well is considered as an obstacle in uniform flow distribution causing more probable issues and hotspots in the reactor bed. Increasing the number of the measuring points and nozzles will cause lots of restrictions and obstacles in the flow distribution and catalyst loading. However, without enough number of measuring points, the product quality, and safety level will decrease. In case of breakage, crack or corrosion of the thermo-well, the liquid or gas flows out of the reactor. If toxic, flammable or hazardous medium stream out into the atmosphere, the catastrophe might be unavoidable.

3.2 Pipe-well (rigid) multipoint temperature system

Pipe-well (rigid) multipoint temperature system is the evolution of the traditional method. Using the traditional temperature measurement only temperature of one point can be measured while the multipoint temperature measurement system consists of several sensors inside a rigid thermo-well (pipe-well) to measure the point’s temperature at desired length.

Figures 3.3 and 3.4 show two versions of manufacturing this system; multipoint elements with individual sheaths and multipoint elements with a common sheath. The former is mineral-insulated thermocouples protected by a metallic sheath with different length located in metallic pipe-well. The latter which is also called compact thermocouple multipoint includes a metallic tube in which positive thermo-leg and mineral insulated powder are common and negative thermo-legs with different legs are connected to the common positive leg in the middle of the metal pipe.

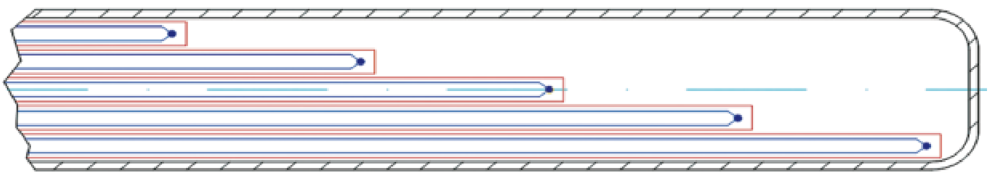

Figure 3.3: Multi-point elements with individual sheaths constructed by Endress+Hauser.

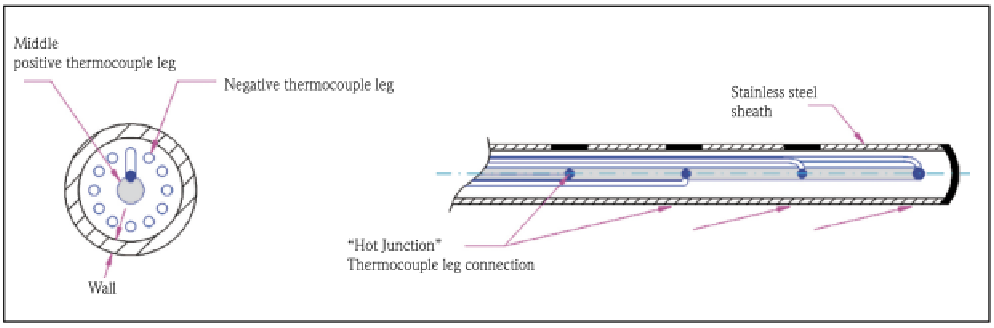

Figure 3.4: Multi-point elements with common sheath (compact fitting) constructed by Endress+Hauser.

A rigid multipoint temperature system with the axial or radial arrangement inside the reactor or vessels enables the process operator to monitor more points than traditional method. Online replacement of measuring elements with individual sheaths shown in Figure 3.3 is possible inside the thermo-wells of rigid multi point systems even during ongoing operations. Several methods to fit the thermo-elements inside the thermo-well are available in the market, for instance, guided tube, compact, bimetal spring (Figure 3.5) and washer disk type (Figure 3.6).

Figure 3.7 shows a pipe-well multipoint thermometer manufactured by WIKA. Since the sensors contact the thermo-well body, the distance between the sensor and catalyst is decreased providing faster response time.

Having the connection point with the pipe-well is possible with guided tube thermo-well and bimetallic spring pipe-well guiding the element tip towards the wall.

During the design, the type of element fitting is clarified based on required measuring points, response time and accuracy. Furthermore, nozzle size and allowable thermo-well diameter penetrating the reactor or vessel impact the selection of thermo-well type. On the other hand, if the reactor content includes hazardous substances, a sealing system is required to avoid spreading of the contaminant to the environment. This sealing system is considered as a limitation affecting the fitting type selection and the possibility of changing the thermo-elements under reactor operation. The sealing system shown in the Figure 3.8 with letter A restricts the exchange of every individual thermo-element. To remove every element, the junction box and sealing system need to be disassembled which is impossible under operation. It will be even more complicated if many thermo-elements are installed inside the pipe-well. Removing the damaged element and entering the new one at the right position may not be possible. In this situation, the whole assembly need to be changed in case of failure in element or thermo-well.

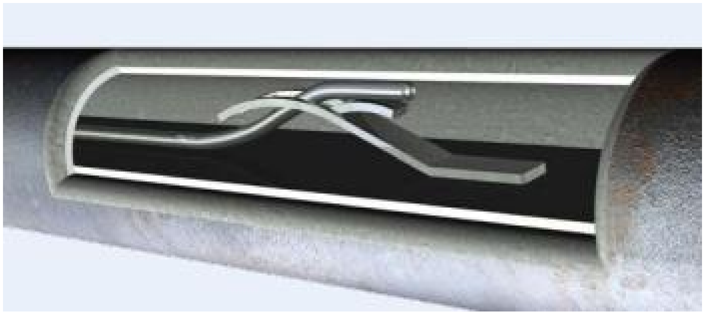

Figure 3.5: Spring loaded band, WIKA-design.

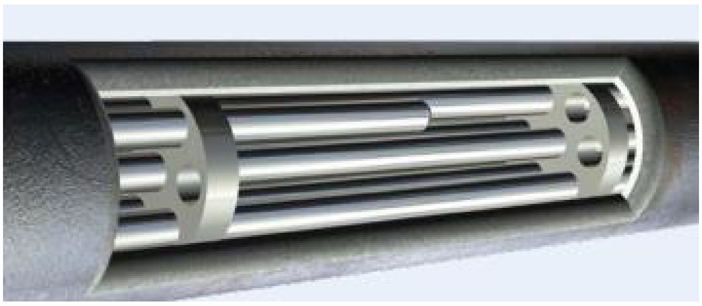

Figure 3.6: Washer disk, WIKA-design.

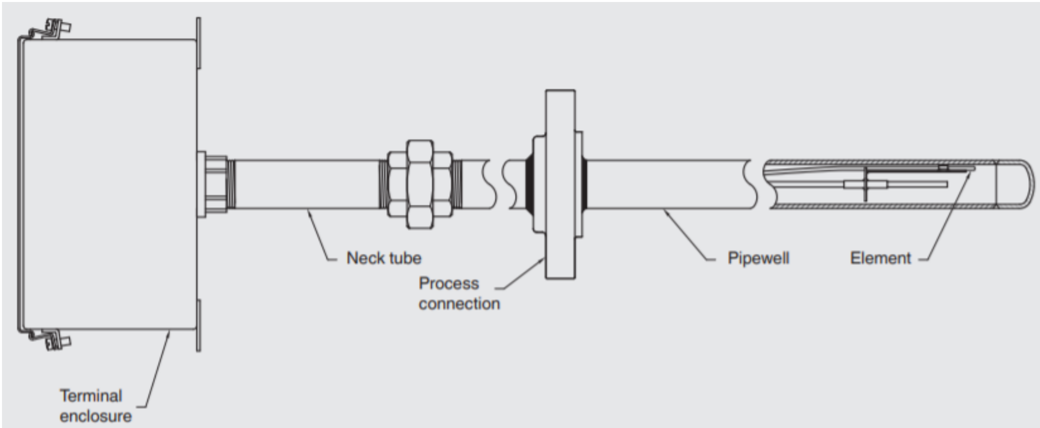

Figure 3.7: Multipoint thermometer with pipe-well made by WIKA.

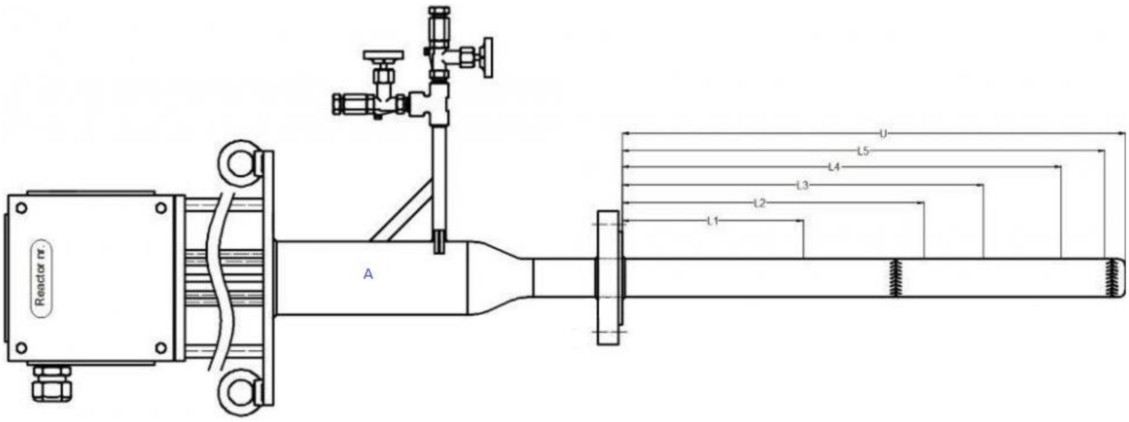

Figure 3.8: Multipoint thermo-well assembly with sealing chamber made by RODAX.

Rigid thermo-well can be installed vertically or horizontally to measure the temperature of vessels and reactors. Vertical installation of this system in multi-bed reactors as shown in Figure 3.9 could cause seal problems in the areas where the thermo-well penetrates the quench zone and distribution tray. On the other hand, since the flow is downward in trickle bed reactors, the probability of channeling and incomplete wetting of catalyst increases.

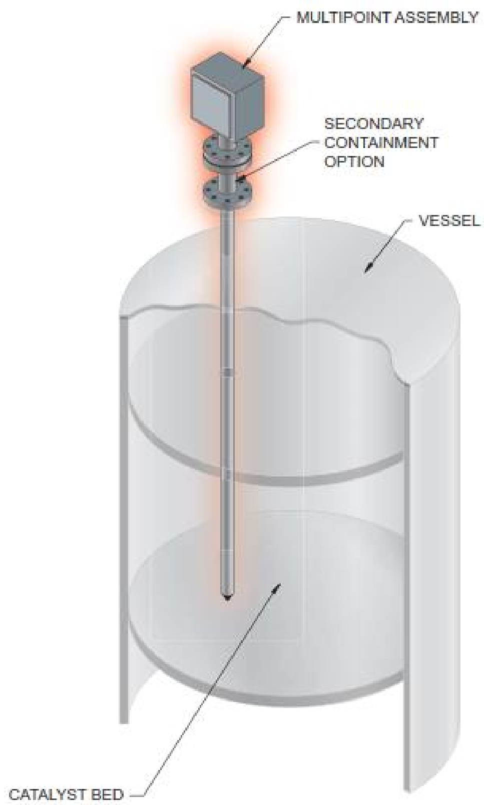

Figure 3.9: Vertically-installed multipoint temperature measurement system inside a protection tube [19].

Figure 3.10 shows a schematic drawing of 4 rigid thermo-wells installed radially in a reactor bed, each thermo-well contains 3 thermocouples. Considering thermocouples with double elements A and B with different lengths, 4 nozzles in reactor wall at the same elevation allow entering of 12 thermocouples to the reactor to measure the temperature of 12 points inside the reactor. This arrangement of thermo-elements monitors the temperature of 12 points at the same level with different angels and radiuses. The more precise monitoring, the more number of thermocouples at different levels and consequently the more number of nozzles are required.

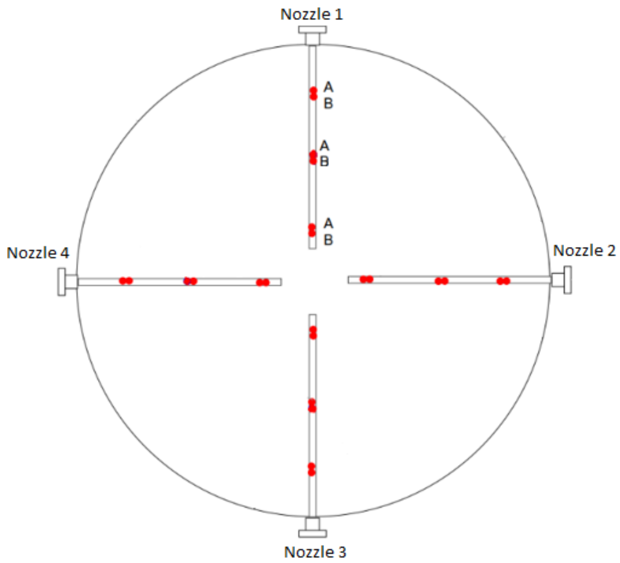

Figure 3.10: Schematic drawing of pipe-well temperature measurement system.

Although this measurement system is used widely in vessels and reactors, below short-comings should be noticed when design and utilization:

- Rigidity of thermo-wells limits the access to every required point. It is restricted to the linear geometry of the pipe-well.
- The probability of flow mal-distribution and uneven catalyst loading in reactor beds due to penetration of thermo-wells and installation supports in distribution trays is increased.
- Rigid pipe-wells along with their fixing supports on the reactor wall may block the flow stream and cause incomplete wetting of the catalyst particles reducing the reactor efficiency.
- Using protective thermo-well prolongs the response time and sensing time of temperature change. Since thermocouples are not in direct contact with the catalyst, heat transfer from catalyst to sensors through thermo-wells is reduced.
- Channeling along the vertical pipe wells may happen. Channeling is flowing the fluid down one section of the reactor like a “channel” and bypassing a large section of the reactor bed. This results in poor mass transfer between different phases and poor product quality as the time is not enough for the catalyst reactions.
- Precision in the entire reactor is low and it has been claimed that differences between two sensors at 427°C might reach more than 12°C. [20]

3.3 1st Generation Flexible Multipoint System

A flexible radial multipoint system provides a profile of horizontal and vertical, axial and radial temperature. This information enables the operator to understand what reactions occur in the reactor and to recognize if and where any problem such as hot spots, channeling or mal-distribution happens.

In 1987, Gayesco International Inc. introduced a new generation of reactor multipoint temperature measurement system to the market. This system was called flexible reactor multipoint temperature measurement system. This system is used in single bed and multi-bed reactors. Thermo-elements consist of MI (Mineral Insulated) with single or double temperature sensors or thermocouples which are routed inside the reactor as shown in Figures 3.11 and 3.12.

Figure 3.11: Schematic routing of Gayesco temperature elements (MI-cable) inside the reactor by WIKA.

Figure 3.12: Mineral Insulated thermocouple cable provided by Ari Industries Inc..

Figure 3.13 shows the seal or safety chamber of the measurement system. The area between primary seal weld and secondary seal weld at both ends of the neck tube called seal chamber. This safety seal chamber is a process barrier to prevent the leakage and escape of process fluid and gases into the atmosphere. A pressure indicator is installed on the seal chamber to detect the leakage from the primary seal weld into the chamber. As shown in Figure 3.14, process fluid leaked through primary seal weld failures into the seal chamber changes the normal pressure of the chamber sensed by the pressure indicator.

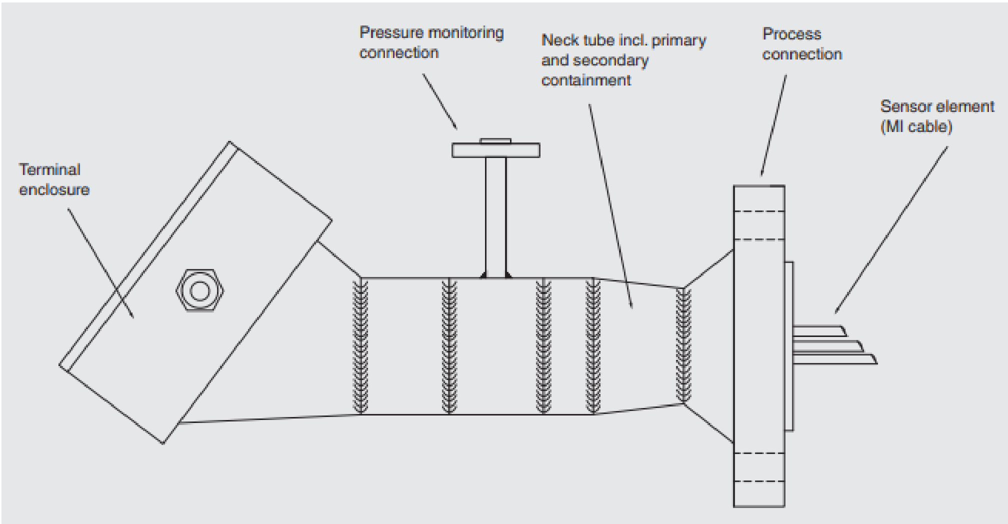

Figure 3.13: Assembly of temperature measurement system made by WIKA.

Not only is the flexible multipoint temperature measurement system equipped with the seal chamber, but also the pipe well or rigid type should utilize it to prevent the process medium and contaminant reaching the outside environment.

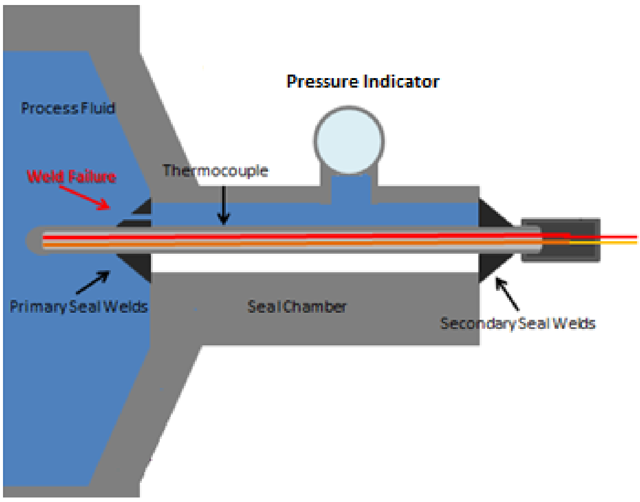

Figure 3.14: Failure in primary seal weld is shown by the pressure indictor, modified Gayesco picture.

Although the pressure indicator is a good approach to display the primary seal welds fault, it cannot detect the cracks and failure of the thermocouple sheath. The process fluid will find a way to reach the environment through the thermocouples as Figure 3.15 shows.

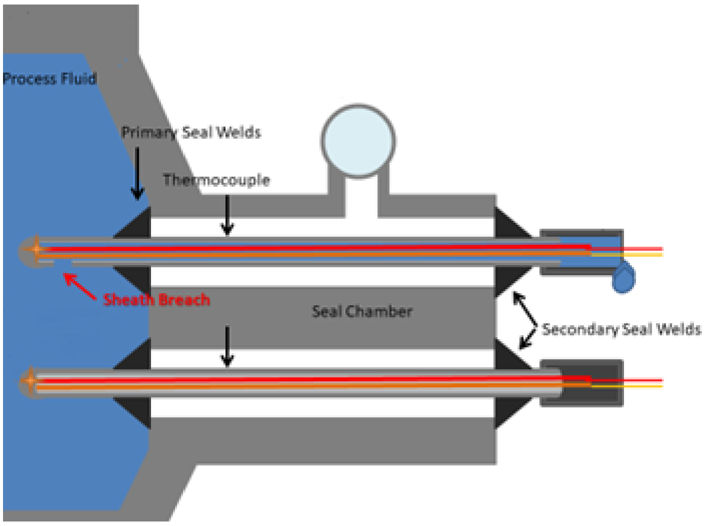

Figure 3.15: 1st generation multipoint temperature system with independent thermocouple sheath, modified Gayesco picture.

Compared with the rigid multipoint temperature system, there are some advantages and drawbacks in using flexible temperature measurement system. It seems the fixation system for installation and supporting of thermocouples in the process flow have less potential of liquid mal-distribution and channeling. The supports made for this measurement system need to carry less weight than rigid pipe-wells, so they will be smaller and tinier.

Due to eliminating the pipe-wells, radial multipoint temperature elements have shorter response time. There will be enough time to take appropriate counteractions and prevent runaway conditions. The flexible elements can be freely routed to the required measuring points radially and axially. This system provides a higher point density which creates a greater visible area inside the reactor. The number of reactor nozzles is considerably decreased, according to Gayesco datasheets, around 40 measurement elements can enter to the reactor from only one reactor nozzle of 3 inch diameter.

Contrast to the rigid multipoint temperature, on-line removal and replacement of failed temperature elements are not possible. Thermocouples and MI cables can only be calibrated and repaired when the reactor is emptied from the catalyst. However, this is an advantage of the rigid type in some rare cases with very few elements inside the thermowells and without sealing chamber.

There is no visible improvement in temperature sensor reliability. Increasing the amount of temperature sensors to offset the rate of failures leads to significant amount of installation support, metallic bars, and fixed structures. Extra installation support and fixation parts inside the reactors increase the probability of undesired issues such as uneven catalyst loading and process flow. Precision level for this system is higher than rigid system yet acceptable up to 12°C. [20]

3.4 2nd Generation Flexible Multipoint System

A new design of flexible temperature measurement was entered to the market by Daily Thermetrics Corporation in 2001. The bed temperature in this system is measured by the flexible probes. Each probe consists of up to eleven independent isolated temperature sensors. Similar supports and structures used for installation of 1st Generation multipoint inside the reactor maintain the probe positions. Installation of probe supports at different levels of the reactor can increase the visibility and make a temperature profile. [20]

Using the 2nd generation of multipoint temperature measurement systems decreases the amount of nozzles and nozzle size on reactor wall. Up to 48 temperature elements can enter through a 1” nozzle [20]. Reducing the hardware for the temperature measurement system and its supports decreases the amount of penetration in vessel and reactor bed considerably.

Similar to rigid pipe-well and 1st generation, a sealing chamber is utilized to prevent the pollutant spreading in the atmosphere. Due to having several elements in a sheath, less seal welding in the seal chamber is needed for the system decreasing the risk of the leakage due to weld failure.

The main difference between 1st and 2nd generation of multipoint temperature systems in the number of elements can be arranged in one sheath. One or two thermocouples suffer from sheath breach of 1st generation while in 2nd generation system, all thermocouples inside the common sheath fail as contaminants move through the cable. Failing all sensing points at once when the outer sheath of probe is broken can be considered as a drawback. The contamination moves through the cable and all thermocouples will be useless simultaneously. Although one probe measures several points, only one crack on the outer sheath can be a potential danger to disappear all measuring points at the same time. Using less thermocouples inside one common sheath is preferable in harsh and aggressive environment. Whereas the more thermo-elements in non-aggressive environment provides a wider temperature profile with less hardware.

3.5 Fiber-optic temperature measuring lance

Fiber-optic multipoint temperature measuring lances determine temperatures and temperature profiles based on Fiber Bragg Grating (FBG) technology. FBG sensors are optical sensors developed to measure the physical parameters like strain, tension and temperature. FBG sensors as an array of independent sensors are mounted on the length of the same fiber optic cable. The sensors are fabricated at the core of the optical fiber reflecting light with defined wavelengths. The Bragg wavelength is essentially calculated by equation (1). [21]

$$\lambda_B = 2.n_{eff}.\Lambda \qquad (1)$$

where

λ_B = Bragg wavelength

n_{eff} = effective refractive index of the fiber core (unstrained condition)

Λ = Distance between the gratings, also known as grating period

Figure 3.16 shows the FBG sensor schematically and illustrates how the light passes or reflects through a FBG sensor.

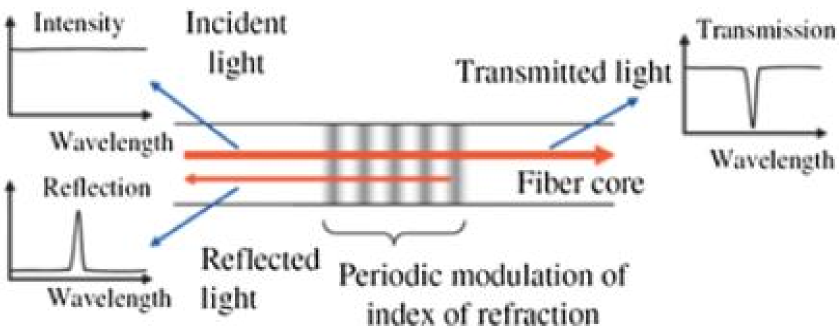

Figure 3.16: FBG sensors reflect the light of a specific wavelength and transmit all others [21].

The wavelength of the FBG reflected light changes as function of temperature and/or strain which allows determining the temperature or strain from the reflected light. FBG wavelength is sensitive to strain and temperature at the same time. Changes in temperature and length shift the FBG reflected wavelength. The amount of this shift is given by equation (2). Studies and experimental results state that there is a linear relationship between wavelength shift and the strain. Similarly, the FBG wavelength shift exhibits good linearly due to the temperature change. [21]

$$\Delta\lambda_B/\lambda_B = (1 - p_e)\cdot\varepsilon + (\alpha_\Lambda + \alpha_n)\cdot\Delta T \qquad (2)$$

where

$\Delta\lambda_B$ = wavelength shift
λ_B = original incident wavelength
ε = expansion of the grating
p_e = photo-elastic coefficient
α_Λ = thermal expansion coefficient
α_n = thermo-optical coefficient
ΔT = temperature change

As an example, the temperature measuring lance; SITRANS TO500, made by Siemens Company consists of the transmitter, and the measuring lances. Each lance is connected to up to 48 temperature sensors on the transmitter at four channels. With up to four measuring probes, 192 measuring points can be processed simultaneously. These sensors are mounted at defined measuring points on the lance. The SITRANS TO multipoint measuring lance or probe showed in Figure 3.19 consists of an optical fiber in which the Fiber Bragg Grating has been embedded. The transmitter sends light with a wavelength between 1500nm and 1600nm generating from a tunable laser to the fiber-optic sensors and evaluates the reflected portions. The fiber is covered by a stainless steel capillary. The multipoint measuring lance with the maximum length of 20m is inserted into the measurement environment in a protective tube on the process side. This system can measure up to 400°C depending on the measuring probe type and some specific probes till 800°C. The diameter of the probes is usually less than 2mm and the distant between the FBG sensors can be selected depending on the process requirement. Minimum distance between sensors is 50mm and maximum 20 sensors can be arranged in the lance. Manufacturer has strongly recommended to avoid direct contacts of the sensors with aggressive chemicals like halogens, nitrogen oxides (NOx), and sulphur oxides (SOx). Besides, mechanical shock and concentrated pressure damage the multipoint measuring lance. [22]

Figure 3.17: Rolled-up SITRANS TO measuring lance made by Siemens [23].

Due to extremely thin design, this measurement system is ideally suited for space constrained applications. The application of this type of measuring system is to monitor the temperature in capillary and micro-reactors, tube and tube bundle reactors, distillation and rectifications. [24]

According to equation (2), the amount of FBG wavelength shift is a function of both temperature and strain.

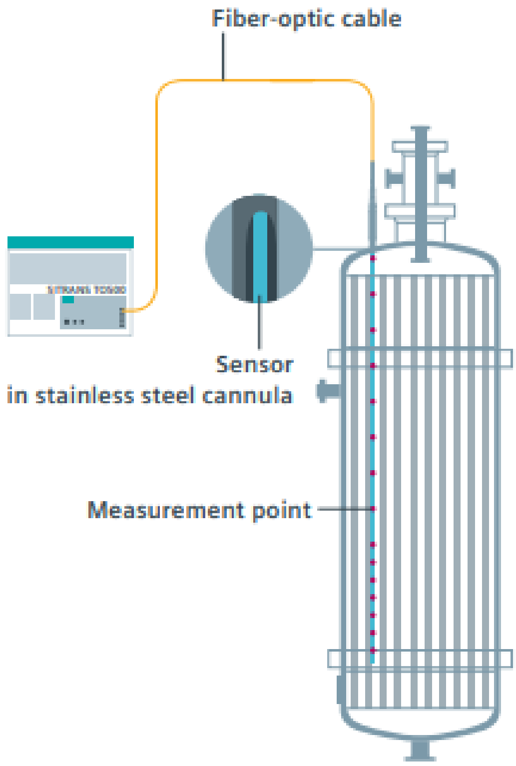

Figure 3.18: Measuring schematic of the fiber optic probe along the reactor tube [24].

Studies show this type of sensor is sensitive to mechanical stress and strain [21] which means installation under stress, curving, and bending influence the temperature measured by FBG sensors.

Compared with other measuring systems mentioned earlier in Section 3, this temperature measurement sensor is not susceptible to corrosive environment due to nature of the glass. However, the cover of fiber optic and protective tube of the lance has to be selected properly, since it can be fractured and corroded which may cause stress and mechanical impacts and glass breakage. The idea is to not install this type of measurement in harsh environment, but future studies may provide a protective method to apply it in aggressive environments.

The location of each sensor and the distance between the sensors are specified to provide more accurate temperature profile. The number of sensors can easily be increased without increasing the cable diameter. This is a unique feature of FBG sensors while the diameter of mentioned types of temperature measurement increases by adding the number of sensors and it is also limited by the nozzle size and manufacturing possibilities.

Fiber optic technology is used in some vessels in oil and gas industry but it can be an interesting topic in sensing application in different types of reactors. Although several literatures show accomplished study and experiment on the operation of this type of temperature measurement in nuclear reactors and nuclear environment [25], there is no evidence if there has been any research on chemical multi-bed reactors. It is proposed for the future, the operation of this type of temperature measurement in hydro-processing reactors to be studied to find out the impacts of the reactants and reaction on the FBG sensors and fiber optic cable. Additionally, since bending the sensors is not allowed due to influence of strain on the measured temperature, the best installation method in multi and fixed-bed reactors and multi-phase reactors needs to be studied.

3.6 Surface temperature measurement

Operating at high pressure and temperature, makes critical vessels and reactors vulnerable to fail at degraded joints and refractories which could increase the risk of unsafe operation and its consequences. Skin or surface temperature measurement is a solution to protect the surfaces from overheating and monitor the extreme temperature and critical points on the reactor or vessel surfaces in refineries and other industries. Recognized challenges for reactor or vessel wall temperature measurement are difficult installation, replacement and wall welding limitations.

Temperature measurements are required in critical vessels and reactors to ensure safe and controlled operations. The number of temperature measurement points inside the reactor depends on the desired level of operational functionality; amount of information needed for reactor troubleshooting and desired level of redundancy. However, the number of elements can be reduced based on the desired level of operational functionality and inner measurement points near the reactor wall can be replaced with reactor skin measurements.

3.6.1 Traditional surface temperature measurement

Traditionally, skin temperature sensors are connected to the reactor or vessel surface with a basic weld tap or washer thermocouple as shown in Figure 3.19. There is no direct contact between the sensor and reactor or vessel wall. Sensors are in contact with the surface by means of welded pad or threaded stud. These two types of sensor design are cheap and common but challenging when installation and replacement the sensors. Usually the vessels or reactors are insulated after welding and installation of theses sensors. Welded pad type is used when the welding and re-welding on the wall are allowed. Related to washer type if the stud is broken, new welding is required on the reactor body, otherwise changing the thermometer does not need a new welding.

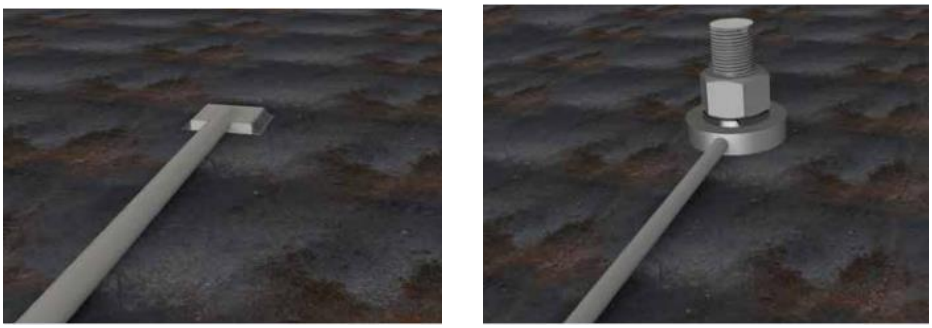

Figure 3.19: Welded pad type (left-side photo) and washer type (right-side photo) sensor made by WIKA.

Temperature sensors can be connected directly to the reactor or vessel wall by the magnet if the surface is ferritic. While minimizing heat transfer, magnetic non-welded sensors are installed and changed at their locations quickly as there is no need for hot-work and successive welding. This type of sensors allows increasing the density of sensors on the surface and enhancing the accuracy due to direct contact with the surface. It should be noted that the magnet has to be strong enough to stick to the wall and provide an optimum contact for the sensor lifetime.

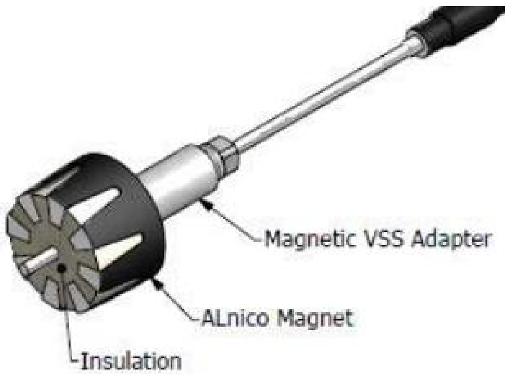

Figure 3.20: Magnetic Vessel Skin Sensors made by Daily Thermetrics.

3.6.2 Infrared imaging system

Infrared (IR) imaging system or infrared thermography is non-contact and real time temperature measurement of the body of the reactors and vessels in oil and gas industry using the infrared technology. This contactless technology provides temperature measurement of moving, hazardous and physically inaccessible surfaces not only in oil and gas industry but also in medical applications or other industries such as minerals and metals.

Infrared thermometers detect the infrared radiation emitted by the object with a temperature above absolute zero (0 K, -273.15 °C). Based on physical principles and without the need for physical contact, the surface temperature of objects using wavelength and intensity of emitted electromagnetic radiation in the infrared region of the spectrum can be calculated. Infrared radiation is a form of electromagnetic radiation with a wavelength between visible light wavelength and 1mm as shown in Figure 3.21. Two parameters of intensity and wavelength at the highest intense change with the surface temperature of the object. Equation (3) shows, according to Planck law, how the intensity of the radiation at any particular wavelength varies with the surface temperature and wavelength for a perfect emitter so called a black body. [26]

$$Q_\lambda = A/ (\lambda^5 (e^{(B/\lambda T)}-1)) \tag{3}$$

where
Q_λ = Intensity (W)
λ=wavelength (m)
A=3.742 x 10^8 W. $\mu m^4 \cdot m^{-2}$
B=constant and 1.439 x 10^4 μm. K
T=surface temperature (K)

Wien’s displacement law states that the temperature rise of the object surface increases the frequency and decreases the wavelength of the peak of the emission. [26]

Infrared measuring devices include lens and detector. Lens focuses the intensity of emitted radiation from the surface of the object on to a detector which converts the intensity to electronic signal.

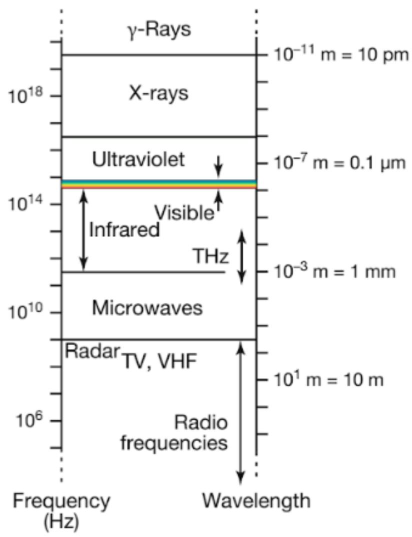

Figure 3.21: The electromagnetic spectrum [27].

One example of this technology is TermalSpection CVM made by Lumasense Technologies. This is an infrared imaging system for real-time temperature monitoring of critical vessel and reactor shells and identifying hotspots, refractory degradation and unusual temperature change which may cause catastrophe. Up to 24 cameras installed in the plant are connected to a computer. This computer, through software, sends the commands and collects the data from the cameras. It can directly be connected with the plant control system. [28, 29]

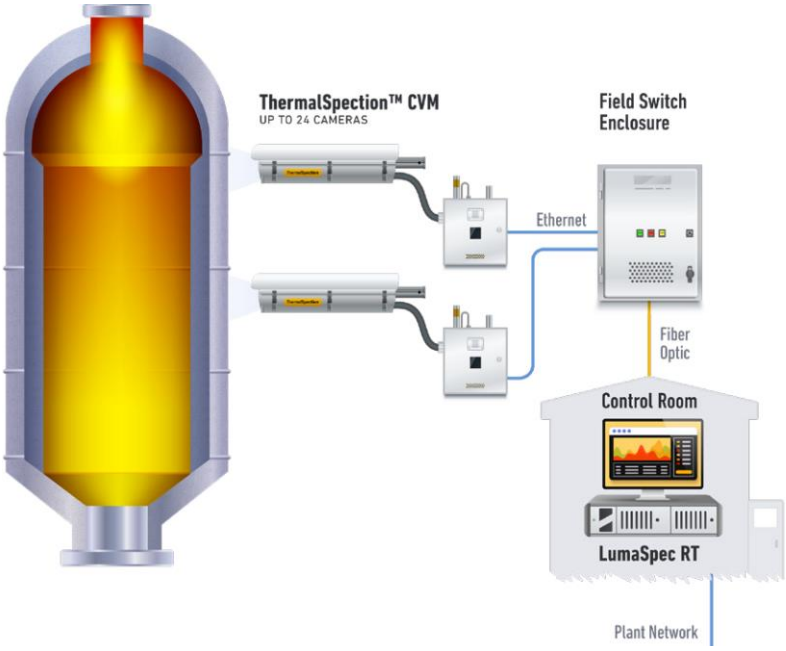

Figure 3.22: TermalSpection CVM made by Lumasense Technologies [29].

A similar system using the same technology is used in industries such as cement, lime, refractories, iron ore, and aluminum production to monitor the skin temperature of the kiln. In these industries, the kiln rotates and a thermal scanner provides a full temperature profile of the kiln. This shell scanner monitors and warns the hotspot at the earliest sign.

Hot spot in the rotary kiln occurs when refractory bricks are separated from the wall and fell inside the kiln. The melted material will be in direct contact with the body and the temperature will increase. In order to protect the kiln, prevent the product interruption and avoid reshaping of the kiln body and extend its lifetime, temperature monitoring of the shell is necessary. Cameras of Kilnscan made by HGH are able to cover the kiln shell with the viewing angle up to 140°. The cameras are installed such that to cover all the area need to be monitored. Figure 3.23 shows how a kiln scanner monitors the temperature of the kiln shell and how it can detect the hot spot formation in real time.

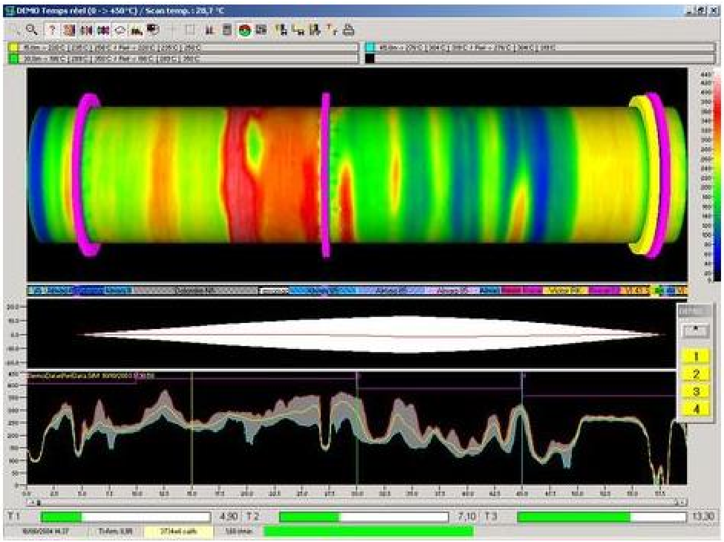

Figure 3.23: Rotary kiln thermal scanner made by HGH.

The IR imaging systems are durable since they have no contact with the process media, and they are not in exposure of contaminants, hot temperature and high pressure. These systems scan the surface of the object fast in real time without any impact on the object or process.

IR imaging systems cannot be applied in insulated reactors since it does not give any information about the reactor inside. On the other hand, insulation layer is a hindering object between the sensor and reactor body which limits and absorbs the radiations from the reactor shell.

4. CHALLENGES OF TEMPERATURE MEASUREMENT SYSTEMS

The purpose of measuring the temperature inside the reactor beds is improving the reactor operation by detecting temperature of the bed and temperature rise over catalyst beds, preventing destruction or deactivation of the catalyst due to hotspots and overheating, monitoring liquid distribution at the top of the catalyst beds and potential channeling within the catalyst beds.

Reactor temperature measurement challenges and complexities are presented in this section in addition to disadvantages of different methods used for monitoring the temperature of the reactors mentioned in the previous section of this thesis.

More or less, these are common challenges for internal rigid multipoint temperature measurement system and 1st or 2nd generation temperature measurement systems in reactors. Sensor type, sheath material of the thermo-elements for 1st and 2nd generation of multipoint measurement systems and thermo-well material for the rigid type, the number of thermo-elements in one sheath or in a thermo-well need to be clarified according to design and operating condition of the reactor. The whole number of thermo-elements and their locations inside the reactor are crucial and critical points in design and manufacturing of the reactor.

Extra challenges and risks of multipoint temperature measurement systems are related to temperature transmitters. If the temperature transmitters send irregular temperature rising or falling to the process control system when sensors are not working properly, amplitude and duration of some uprisings might be enough to activate and trip the interlock functions.

The number and location of required thermocouples and elements have been challenging issue in different aspects. The leakage of process medium into the atmosphere jeopardizes the safety and pollutes the environment. Economically, time duration needed to replace the elements during shut down decreases the profit. The probability of happening these issues rises with increasing the number of temperature elements. Although reducing the number of thermocouples and elements decreases the time required for element replacement and shut down duration in case of sensor failure, it can impact the controllability of the reactions and safety level adversely.

The number of temperature elements has to be evaluated to give an optimum number of them without compromising the safety and product quality. The number of temperature measurement points inside the reactor depends on the desired level of operation, functionality, and level of redundancy.

When the cracks and corrosion damage the sensors, process liquid and flammable or toxic gases stream out of the reactors through the MI cables. MgO compact powder is getting washed and solved in the process liquid and will be a passing way for the leakage inside the sealing chambers or even electrical junction boxes. Increasing the safety level is possible by using a pressure measurement to indicate the cracked and corroded elements and prevent the leakage of flammable gas and pollutants into atmosphere. It should be noticed, specifically in hydro-treating, that high amount of hydrogen, CO_2, etc. exist in the reactor and a proper system with a high level of safety needs to be provided. Process leakages into atmosphere or seal chamber can also happen through welding in primary seal if is not well-conducted or is corroded. Process fluid leaked inside the seal chamber either through sensor breach or welding faults has lower temperature than the process media inside the reactor. Since the sealing chamber is located in ambient temperature, the temperature of its inside surface is lower than the temperature inside the reactor and process fluid. This temperature difference results in condensation inside the sealing chamber. Due to condensation, the media inside the seal chamber which is mostly hot aqueous solution with chloride expedite the corrosion. Microscopic cracks in welded parts and using improper material in welding lead to this problem. Non-destructive testing (NDT) is essential to detect the pores and cracks before and during installation of the system.

Figures 4.1 and 4.2 illustrate the corroded, cracked and broken sheath made out of different materials. Upgrading and changing the sheath material is proposed as the permanent solution to avoid similar problems. Not every material can be used in every environment. In case of wrong selection of material, even double sheath which sometimes is offered by the manufacturers cannot withstand against corrosive contents. Being familiar with the metals and alloys, is really important since even different grades of the same alloys have different properties and show different behaviors in the same process condition. For instance, working condition and mechanical properties of Inconel 625 grade 1 and grade 2 differ.

Figure 4.1: Broken temperature element sheath made out of Incoloy 825.

Figure 4.2: Cracked and corroded cable sheaths made out of SS347.

5. ANALYSIS AND SOLUTIONS

Observations on the petrochemical industries and oil refineries often show challenges in reactor temperature elements. Due to harsh and aggressive conditions, these devices are frequently problematic. On the other hand, since the product quality, cost effectiveness and safety are highly demanding, the reactor temperature measurement system is on increasing focus.

Pipe-well multipoint, 1st and 2nd generation of multipoint and skin temperature measurement systems introduced in Section 3 are usually applied in different vessels and reactors in oil and petrochemical industries and power plants. Considering their advantages and drawbacks, it might be challengeable to select what type is suitable for which vessels or reactors. Some essential factors would be the design type and size of reactor, the number of beds and nozzles, type of reactions occurring inside the reactor and process requirement for temperature monitoring.

In bio-mass co-processing, in addition to the affecting factors on selecting the temperature measurement system, feedstock composition needs to be noticed. The feedstock containing oxygen, chloride and organic elements and components impacts directly on the reactor environment and consequently material selection.

High pressure, exothermic process, high consumption of hydrogen, corrosive and aggressive environment inside reactors require special design and specific material and equipment [6]. Recently, the catalyst manufacturers have improved the activity of catalyst. These catalysts have better conversion rates; while raising productivity and profitability levels they can result in a quicker reaction. Hydro-treating reaction of bio feedstocks is strongly exothermic which can cause the reactor runaway. The new generation of highly active catalysts accelerates reactions. Exothermic reaction in presence of a high-activity catalyst has to be controlled precisely to avoid thermal runaway. As a consequence of quick temperature rise above the metallurgical limit of the reactor wall, reactor explosion and environment contamination strike.

To improve the product quality, reactor functionality and safety level of operation, the number of temperature elements needs to be increased. In contrast, high density of temperature elements inside the reactor requires more fixing supports which have a negative impact on flow rate, fluid distribution and finally product quality [6]. The number and location of required temperature elements need to be studied and optimized to monitor the temperature inside the reactor properly. The fact is, the estimation of which point is more crucial or is in higher risk of hot spots or other issues is impossible.

The reactor temperature needs to be scanned all the time to monitor the unusual temperature. None of the available manufactured temperature measurement systems for reactors are able to scan the temperature of the reactor internal volume and provide a real time profile of temperature. Only predefined points are sensed by the thermo-elements which is not really an appropriate approach to detect the issues regarding local temperature rise, mal-distribution, etc. According to the temperature profile showed in Figure 2.4, the hottest sections are the bottom of the reactor beds. Although the hotspots can happen at every point of the reactor, the hotspot at the bottom of the reactor bed may cause runaway in a shorter time. This means locating more elements at these levels is necessary for the safety and desired utilization of the catalyst. On the other hand, by comparing the measured temperatures at the lowest level of this section, RTD and mal-distribution of the fluid can be identified.

The sensor sheathes are all directly contacting the process fluid and catalyst while under dynamic stress, mechanical tension, vibration and turbulent current of the fluid. Moreover, when introducing the bio-based feedstocks to the process, new products and byproducts have additional influence on the sensor functionality and material selection. There is no non-contact temperature measurement system in the market to measure the reactor temperature. Introducing a new contactless sensor and real time temperature measurement system can be considered as a research topic for the future. The main reason hindering the research route might be the gap existing between industry and technology. The researchers should know the exact need of the industry to improve and work on the existing devices.

The pipe-well material, sheath material and installation method can influence the precision and reliability of the temperature elements and consequently on reactor operation and interlocking actions. Below subsections explain how to select thermocouples and sheath material as the most challengeable criteria to have a better monitoring of temperature inside the reactors. This study focuses on the sheath material of MI-cable and suggests the most suitable material for the harsh environment.

5.1 Temperature measurement system

Among available types of temperature measurement systems, the most suitable temperature measurement system for this application can be a combination of surface temperature measurement system and multi element temperature measurement systems. Skin (surface) temperature sensors detect the abnormal wall temperature to prevent reactor metallurgical issues. Usually, there is no major issue in using this type of sensors, since these sensors are installed outside the reactor on the wall and are not affected by the process fluid and reactants. Therefore, there is no limit in selection of any type of surface measurement except temperature range and maintenance provisions.

Using the skin temperature elements can also reduce the number of elements inside the reactor based on the allowable level of operational functionality. Temperature elements measuring the points beside the reactor wall can be substituted by skin measurements. However, the skin temperature does not give useful information about the reactor inside and is considered an additional protection for the reactor shell.

Selection of multipoint temperature measurement systems; pipe-well type, 1st or 2nd generation depends strongly on the reactor structure, reactions, severity of the environment, design and operation process data.

Error in measured temperature activates interlocking functions and even unexpected shut down. Fortunately, modern temperature transmitters are equipped with advanced diagnostic capabilities and are able to recognize the sensor faults and sensor sheath breach. In order to avoid spiking fault and unnecessary shut down, temperature transmitter with related features needs to be utilized.

Assuming use of the 1st generation of temperature measurement system, double elements have to show almost the same temperature. The extraordinary temperature detected by one out of two thermocouples inside one unique sheath, if no obvious change senses by the adjacent elements points a damaged sensor out. It is abnormal situation as the measured temperature has to be almost equal in both thermocouples in the same MI cable and to be sensed by the elements installed nearby. The transmitter has to have self-diagnostic features to detect the sensor fault. Otherwise, there is no chance to check the sensor till unloading the catalyst, visual inspection and X-Ray test to see if cracking and corrosion have affected the thermocouple sheaths or if sensor re-calibration is required. This type of failure which is sensor fault needs to be identified by the transmitter, as sensor faults can transfer wrong signals to the control system causing trips.

If temperature transmitters connected to thermo-elements send invalid measured temperature to the control system and the process media is emitted outside of the reactor, the element sheath has surely been corroded or cracked and the media has streamed out of the reactor.

New and smart temperature transmitters are compliant to the Namur NE 43 recommendation. The transmitters with Namur NE 43 feature are able to separate the instrument faults from process measurement. For the latter, it usually uses the 3.8 to 20.5 mA signal range. To indicate the failure, signals ≥21 mA or ≤3.6 mA are used. According to Namur NE 43, the transmitters should detect and signalize the thermo-element failure (breach). Transmitters are configured to drive the output signal (under 3.6 mA or above 21 mA) in case of failure and signal out of process range. The process control systems recognize this value as a failure state and generate an alarm.

When the signal is in the process range but different than temperature measured by the sensors nearby hints a sensor fault which the transmitters are not able to recognize. False signal is originated from the sensor fault, but the transmitter forwards this false signal without recognizing it as a fault. This desired diagnostic is required for critical applications either by modifying the transmitters or changes the control system logic.

5.2 Sheath Material

Material selection is a decisive factor impacting the sensor lifespan and reliability of the temperature measurement system. Regardless of precision and reliability of the elements, sheath material selection and sheath wall thickness are the essential steps in choosing the correct system. The wrong or weak selection of sheath and its thickness affects the quality of the product and has the potential to decrease the safety level and cause the reactor runaway and catastrophe.

In this study, the hydro-processing reactor is categorized under aggressive industrial environment with high chloride content. Depending on the feedstock type and process route, different types of impurities might exist in the reactor. H_2, H_2S, HCl, NH_3, free fatty acids, CO_2, CO, and H_2O are potential pollutants inside the reactor. Selected sheath material needs to resist in this harsh environment for the proper operation of sensors.

Austenitic stainless steel SS321, SS347, Incoloy 825, and Inconel 625 are the materials usually used in outer sheaths of thermocouples. Not all these alloys are equally susceptible to erosion, corrosion and cracking in various environments. Hardness, ductility, material composition, and corrosion resistance are some parameters need to be taken into account to choose a proper material.

Environmental condition, temperature, level of tensile stress, deformation rate, presence of chloride, hydrogen and hydrogen sulfide gas, solution pH, metallurgical factors, amount of cold work, and heat treatment affect the susceptibility of alloys to cracking. Stress corrosion cracking (SCC) is a mechanical-chemical process, combination of mechanical stress and corrosion reactions, leading to crack propagation. Environmentally assisted cracking (EAC) occurs when a “susceptible metal microstructure” is exposed to “corrosive environment” and subjected to “mechanical tensile stress”. Removing any of these factors can prevent EAC and increase operational safety. SCC, hydrogen embrittlement (HE), corrosion fatigue, and liquid metal embrittlement are general forms of EAC. [17]

Stainless steels are iron alloys containing more than 10% chromium (Cr) to prevent the formation of rust in general corrosive environment. Alloy composition, structure, thermal history and environment affect the susceptibility of these alloys to stress corrosion cracking. Different compositions show different behavior in a certain atmosphere. Adding a sufficient amount of nickel element to stainless steel (SS) makes the austenitic type of SS which can improve the corrosion resistance. This alloy is used in chemical industries. It has excellent mechanical properties and corrosion resistance. Austenitic SS321 and

SS347 are identified under 300 series type. Chromium along grain boundaries of these alloys has less tendency to combine with carbon and forms chromium carbides. Various forms of sulfur even in small quantities in the environment exacerbate corrosion. Hydrogen sulfide and sulfur vapor are more aggressive than sulfur dioxide. To resist in hydrogen sulfide atmosphere with high pressure, chromium content needs to be at least 17%. Most austenitic grades are resistant up to 204°C in liquid sulfur while SS321 and SS347 can resist to 444°C. [30]

Austenitic stainless steels (ASS) exhibit SCC in hot, concentrated chloride solutions and chloride-contaminated steams. Chloride ions promote SCC in aqueous environment for austenitic stainless steel alloys. Since the stainless steel alloys are sensitive to chloride induced localized attack like pitting and crevice attack and stress corrosion cracking, they cannot be used in hydro-treating reactor condition [30, 31]. Austenitic stainless steels are susceptible to SCC in the presence of hot aqueous solutions containing chloride ions. This feature and weakness in chloride atmosphere will cause corrosion and cracking on the thermocouple sheath. This alloy shall not be used as the sensor sheath inside the reactor as it cannot tolerate the harsh nature of chloride ions in reactor environment.

Duplex stainless steel alloys offer several advantages over the austenitic stainless steel. Types 329 and 2205 are usually resistant to CI-SCC (Chloride Induced Stress Corrosion Cracking) but not in high temperatures. They are also susceptible to hydrogen embrittlement in temperature about 370°C. [30]

In most corrosive environment, nickel (Ni) alloys perform better than stainless steel as suitable alloy can be made by dissolving specific elements into nickel for a particular environment. Dissolving molybdenum and chromium increases protection against corrosion in reducing condition and oxidizing condition, respectively.

Due to face centered cubic lattice structure of nickel, the family of nickel based alloys have great ductility, formability and malleability. If processing of nickel alloys, such as cold working or high temperature aging decreases the ductility, the probability of hydrogen embrittlement may increase. Hot caustic and hot hydrofluoric acid environment are causing EAC in corrosion resistant nickel alloys and austenitic stainless steel. Since pure metals have lower mechanical strength and great ductility, they can resist more than alloyed metals to EAC. [17]

Nickel-based alloys are categorized as pure nickel, nickel-copper, nickel-molybdenum, nickel-chromium-molybdenum, and nickel-chromium-iron-molybdenum alloys. Each category has its own properties to be used in a specific environment. For instance, pure nickel provides a good corrosion resistance in highly concentrated caustic media compared to composition of nickel, chromium, and molybdenum. Nickel can withstand cold reducing acids while warm reducing and oxidizing acids rapidly attack pure nickel. In hot caustic media, alloyed nickel is preferred to pure nickel. Nickel-copper alloys are mainly applied in pure hydrofluoric acid and are more resistant to corrosion compared with pure nickel in hot reducing and oxidizing acids. Hastelloy B or nickel-molybdenum withstands in reducing HCl media irrespective of temperature and concentration while they cannot be recommended to apply in oxidizing acid. [17]

The largest group of nickel based alloys is nickel-chromium-iron-molybdenum family. Incoloy 800, Incoloy 825, Inconel 600, Inconel 690, and Hastelloy G-30 belong to this group of alloys. These alloys have larger content of nickel than SS316 which makes them more immune to stress corrosion cracking in warm water and chloride media. Nickel alloys prevent SCC in conditions such as hot caustic and wet hydrofluoric acid conditions. Temperature, amount of chloride, hydrogen sulfide gas (H_2S), and environmental condition impact on the SCC resistance of this alloy. [17]

Inconel 600 and Inconel 690 are extensively used in nuclear power plants, their stress corrosion cracking behavior in pure water and caustic solution has been studied in nuclear services. Alloy 600 suffers SCC in pure water with temperature higher than 300°C and it has been found less resistant than Alloy 690. Alloy 825 shows better resistant to sulfuric acid and nitric acid than Inconel 600 because the former consists of molybdenum and chromium which prevent the attack of sulfuric acid and nitric acid. [17]

Due to more molybdenum content, nickel-chromium-molybdenum alloys are more resistant to corrosion than nickel-chromium-iron-molybdenum alloys. It has been reported that high strength nickel-chromium-molybdenum alloys failed by SCC in very harsh condition.

The most common nickel-chromium-molybdenum alloy is Hastelloy C-276 and more advanced ones are Hastelloy C-2000, Inconel 686, and Nicrofer 5923. These alloys can highly resist in both reducing and oxidizing conditions due to containing molybdenum and chromium. This category of alloys is also the most resistant to chloride-induced corrosion. Studies show Hastelloy C-276 can be applied at any chloride concentration and at any partial pressure of H_2S and CO_2 up to 260°C. This alloy might be so susceptible to the presence of element sulfur in the environment. [17]

Alloy Inconel 625 is a nickel-chromium-molybdenum-niobium alloy produced in two grades. Annealing of this alloy at 950 to1050°C produces Grade 1 (soft-annealed) to be applied in a temperature range between -196 and 450°C whereas Grade 2 (solution-annealed) annealed at 1080 to1160°C is suitable for applications with operating temperature between 600 and 1000°C. Inconel 625 is one of the best alloys withstanding sea water and marine conditions. It often acts as cathode in presence of other materials in sea water. Alloy 625 shows good corrosion fatigue strength in sea water. [32] These alloys are resistant to cracking in solutions with hot and high chloride aqueous while caustic solutions, water and hydrofluoric acid in higher temperature may cause stress corrosion cracking.

Reports show intergranular cracking in Hastelloy C-276 and Inconel 625 by exposure to aqueous solutions near the critical point of water (347°C). [17]

A wide spectrum of material is used in oil and gas industries. The materials suitable for corrosive environment are divided into several groups including martensitic stainless steel, duplex stainless steel, austenitic stainless steel and nickel based alloys. Mechanical properties and corrosion resistance are two main factors for alloy selection. Stronger alloys are more susceptible to SCC and Ni-alloys with more chromium and molybdenum contents are more resistant to corrosion. In addition to alloy composition and microstructure, environment conditions such as partial pressure of H_2S, pH, chloride concentration, oxygen, carbon dioxide, elemental sulfur, and temperature affect the cracking resistance of alloys. Usually, Ni-based alloys are selected for the environment with H_2S and chloride contents with temperature more than 200°C. [17]

MI cables are mostly cracked and ruptured at the bends and are subjected to stress corrosion cracking. It seems no single mechanism leads to MI cable fracture, but also several factors such as cold work, hydrogen embrittlement, impurities, and corrosive environment can cause cable fractures. The corrosion and cracks might happen due to improper material selection and cold deformation and over bending of the probes during installation to form the final shape and route of the cable inside the reactor.

According to mentioned explanations, it seems the most suitable alloy to use in the reactor environment is not such that easy to be introduced as a result of this research. Several conditions need to be considered at the same time by material and process engineers. Focusing on just material withstanding reducing and potential oxidizing media in the reactor environment, an alloy from the nickel-molybdenum-chromium family should be selected.

The selected alloy has to resist against SCC in reactor temperature and in the presence of nitrogen, chloride ions, and hydrogen sulfide. On the other hand, it needs to have higher ductility to tolerate formation and bending inside the reactor.

According to the Table 5.1, Inconel 625, Hostelloy alloys C-276 and C-2000 can seemingly be proposed for oxidizing and reducing applications. Hastelloy C-2000 alloy has a copper addition providing a significant resistance to sulfuric acid better than Inconel 625 and due to higher chromium content, its resistant in oxidizing chemicals is more than Hastelloy C-276. Therefore, Hastelloy C-2000 might be the preferred alloy in hydrotreating reactors, but before manufacturing and installation, required tests on the material to identify its behavior in simulated reactor environment are necessary. Besides, the effects of hydrogen on deformation, fracture and degradation of this material in reactor operating condition have to be analyzed. This could be an interesting topic for future works.

Table 5.1: Comparison of chemical composition and mechanical properties between several Ni-based alloys [17].

Alloy	Approximate composition	YS (0.2%)	UTS	ETF (%)	RH	Application
Commercial Nickel						
Ni-200	99Ni-0.2Mn-0.2Fe	190	450	50	60 B	Strong caustic
Ni-Cr-Mo Alloys						
C-276	59Ni-16Cr-16Mo-4W-5Fe	347	741	67	89 B	Versatile CPI and pollution control
Inconel 625^{A}	62Ni-21Cr-9Mo-3.7Nb	535	930	45	95 B	Aerospace, pollution control
Hastelloy C-22	59Ni-22Cr-13Mo-3W-3Fe	365	772	62	89B	FGD,CPI, nuclear waste
Hastelloy C-2000	59Ni-23Cr-16Mo-1.6Cu	345	758	68	NA	CPI, oxidizing and reducing, Sulfuric
Ni-Cr-Mo-Fe Alloys						
Inconel 600	76Ni-15.5Cr-8Fe	275	640	45	75B	Nuclear Power
Inconel 690	58Ni-29Cr-9Fe	352	703	46	NA	Nuclear Power
Inconel 825	43Ni-21Cr-3Fe-3Mo-2Cu-1Ti	338	662	45	85B	Oil and gas, Sulfuric, Phosphoric

YS = yield stress (MPa), UTS = ultimate tensile strength (MPa), ETF = elongation to failure, RH = Rockwell hardness, CPI = chemical process industry, A = thermally aged, NA = not available

5.3 Installation Method

The required length of the MI cables needs to be calculated before manufacturing and installation. Focusing on installation instruction, bend limitations and material properties when calculation of the length for routing the cable to sensor position is necessary. Longer length of the cable causes extra bends and increases the risk of over bending and sheath breach, fluid blockage, and channeling of the media inside the reactor as Figures 5.1 and 5.2 clearly show.

Figure 5.1: Installation of thermo-elements with extra bending.

Figure 5.2: Over bending of thermo-elements.

Brackets and supporting frames are usually tailor-made to suit the reactor interior and obtain the best temperature location creating a 3D temperature profile. The MI cable fixing supports and frames need to follow the requirements of the process licensor. Some examples of supporting frames made by Thermo-electra are shown in Figure 5.3.

Rounding and shaping the probes over the circular frame to locate the probes at the desired point are unavoidable, therefore, cold work and bending of the thermocouple probes should be conducted carefully following the instructions. Over bending and deformation of the probes will increase the probability of element sheath breach.

The location of nozzles on the reactor wall have to be designed based on the internal reactor design and best installation method for the thermo-elements to minimize curving and bending of the elements.

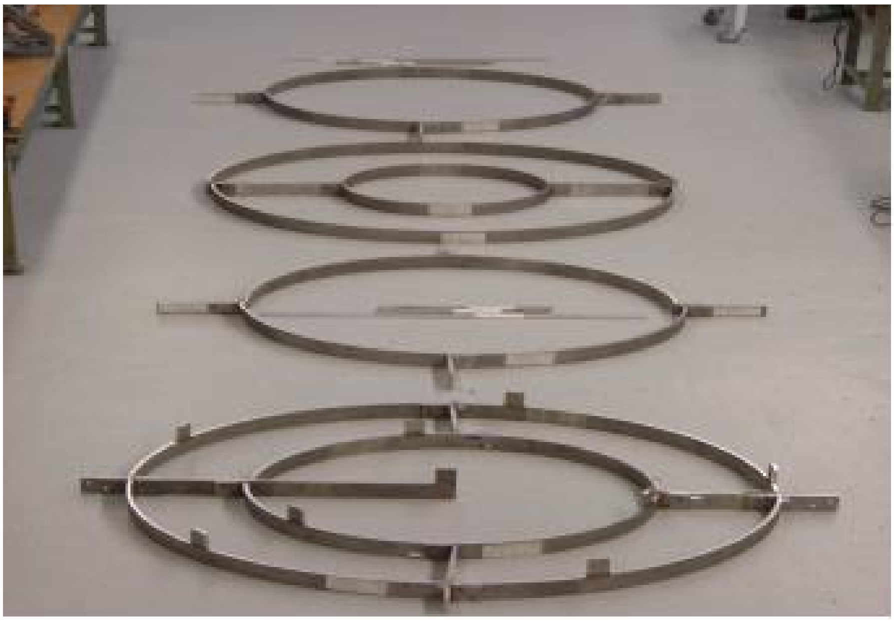

Figure 5.3: Fixing support for multipoint temperature elements made by Thermo-electra.

Figure 5.4 shows how the bended elements are under compression and tension at the nozzle reaching the fixing support. According to Figure 5.5 showing the schematic of nozzle location and fixing support, there are unnecessary bends in blue circles which can be avoided. There should not be difference between the nozzle level and support level, in this way at least 60% of the bends is eliminated.

Figure 5.4: Thermo-elements at nozzle.

In multi-bed reactors, vertical installation should be avoided and vertical sections of the MI cable routing needs to be minimized. These sections may be affected by the thermal extension of the reactor under operation leading to extra stress and sheath fracture.

As mentioned, the routing of cables is tailor-made according to the reactor type and its application, however shadows of the internal structure of the reactor should be used for routing the thermo-elements to reduce the stress over the cables.

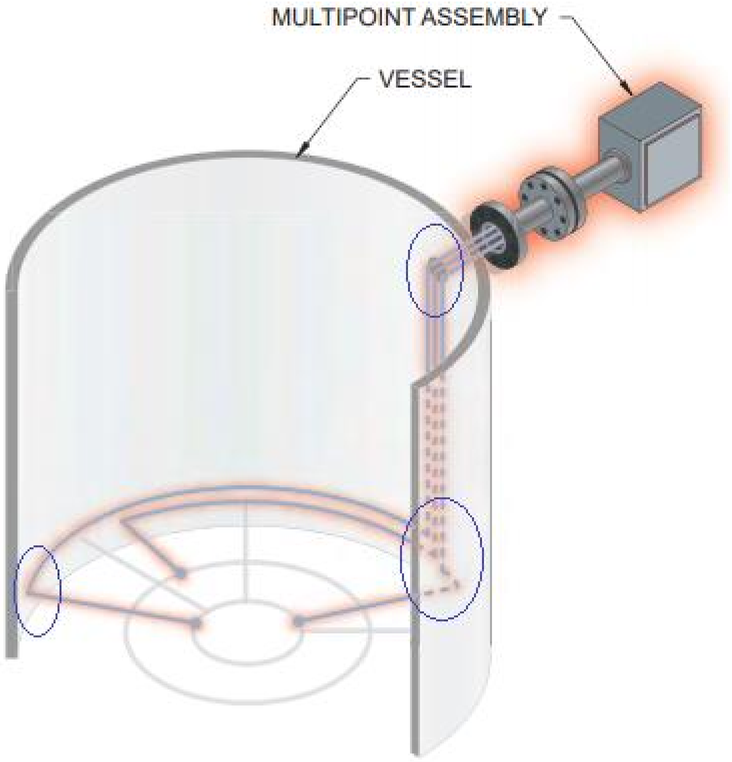

Figure 5.5: Flexible multipoint temperature measurement system [19].

In case of having a vessel, tank, and single-bed reactors, vertical multipoint temperature measurement can be easily selected. Whereas in multi and fixed bed reactors this installation impacts the sealing and reactor functionality.

6. CONCLUSIONS

In order to enhance the efficiency, safety, and product quality in critical reactors and to minimize the risk of hotspot formation, reactor runaway and flow mal-distribution, reactor temperature monitoring is of special importance. This monitoring is also to limit the temperature rise below the maximum allowable temperature. The need for temperature measurement systems is on focus especially when introducing bio-feedstocks to the petro-refinery process units. The reactions are highly exothermic and temperature can rise rapidly which make the reactor a high-risk equipment.

Real time temperature measurement as an ideal solution covers the requirements and monitors the whole reactor in every moment, but no system has yet been manufactured for this purpose. Available methods and systems for reactor temperature measurement use thermo-elements. Every element can only measure one small spot and it is not possible to control the temperature of the whole volume of the reactor.

The challenges are to install a sufficient number of temperature measurement elements inside the reactor beds to quickly detect high temperatures and undertake countermeasures. This can avoid production of undesired byproducts, reactor runaway and more importantly unexpected plant shutdowns, which would otherwise be required due to the complicated procedure for replacing the reactor catalyst.

The reactants, reactor structure along with corrosive environment have considerable impacts on the temperature measurement system selection and operation. According to this research, rigid thermo-well, 1st and 2nd generation of flexible multipoint measurement systems can be utilized in reactors depends on the nozzle location, reactor dimension and process conditions.

The internal structural design of a reactor should consider all conditions, nozzle locations and installation of thermo-element supports to maintain the reactor performance as high as possible and simplify the thermo-elements installation. Otherwise, adverse impact of installation support increases the probability of channeling, liquid mal-distribution, and non-uniformity of the loaded catalyst which in turn wetting regime of particles and reactor performance will be affected.

Sheath material selection of thermo-elements is critical. The wrong material cannot withstand in aggressive and corrosive environment and can jeopardize the safety of the plant. The cracked and corroded sheath is usually problematic issue caused by the wrong selection of the material. The properties of several materials were expounded and compared in this thesis to recommend proper materials in different environments.

The mentioned challenges and restrictions in hydro-treating reactors affect the type, installation method, outer sheath material, and lifetime of temperature measurement systems. Material, primary and secondary seal welding, nozzle configuration and installation method need to be taken into consideration to address the issues and improve safety, reliability, maintainability, and operability of the temperature measurement system.

The type, location and number of temperature elements are defined based on the bed reactor design temperature, temperature ranges, safety requirements, reactor dimension, internal design of the reactor, catalyst type and process condition. The elements locate in the points which are really important to be monitored from the process point of view.

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