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Kinetic studies of MDI synthesis reaction using online IR and Raman spectrometers

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Abstract

Kinetic studies of the reaction of 4,4'-methylendiphenyldiamine (MDA) with triphosgene (bis(trichloromethyl) carbonate, BTC) in chlorobenzene (MCB) were performed at various temperatures in online mode using IR and Raman spectrometry. Thus, the possibilities of analyzing reaction intermediates for subsequent application of these methods in a pilot plant were considered. Individual IR spectra of MDA and MDI in monochlorobenzene were obtained. A method for online control of MDI accumulation during the reaction using IR spectrometry has been developed.

Keywords: *Kinetic studies; Online monitoring; IR spectroscopy; Raman spectroscopy; 4,4'-methylendiphenyldiamine (MDA); Methylendiphenyldiisocyanate (MDI); Phosgenation.*

1. Introduction

The phosgenation reaction of 4,4' - methylendiphenyldiamine (MDA) is one of the simplest ways to produce methylendiphenyldiisocyanate (MDI) [1-2]. In this case, the gaseous phosgene can be replaced with a more convenient solid triphosgene [3-4] (Figure 1).

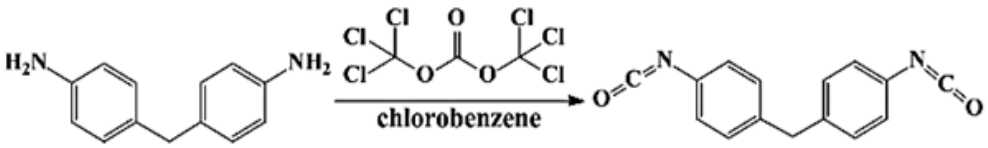


Figure 1. The MDI synthesis reaction

In terms of toxicity, triphosgene is very close to phosgene. Therefore, studying the kinetics of this reaction, direct sampling is significantly complicated. Online chemical reaction monitoring, which is a separate branch of the chemical industry, is widely used to study systems, which are air sensitive, toxic, explosive or being under pressure. Online monitoring allows detecting the start and ending times of reaction, to determine the effects of intermediates, temperature, dosing or mixing rates, and to understand the kinetics and mechanism of the reaction.

For direct sampling, one of the most commonly used analysis methods is high performance liquid chromatography (HPLC), and for online monitoring, FT-IR spectroscopy [5-6], and similar Raman spectroscopy [7-8], are the most suitable. During online monitoring, absorption data (3D spectrum) is tracked over time or converted to concentration values (2D graph) after offline NMR calibration. Based on spectroscopic data obtained in real time, a direct quantitative study of reagents and reaction products can be performed.

Both Raman and FT-IR spectroscopy provide a spectral characteristic of molecules vibrations ("molecular fingerprint") and are utilized to identify substances. FT-IR spectroscopy helps to create trends and profiles of reactions in real time by providing very accurate information about the kinetics, mechanism, reaction pathways and the effect of synthesis parameters on the target product. In this regard, high data density leads to a significant reduction in the

experiments number. An important advantage of IR probes is their ability to work in conditions of low and high temperatures, low and high pressures, in acidic, alkaline, caustic, corrosive and aqueous media, which allows them to analyze wide variety of chemical processes.

Raman spectroscopy provides information about intramolecular and intermolecular vibrations and helps to form a more complete view of the reaction. This type of analysis is sensitive to many functional groups, and it is especially effective for obtaining information about the molecular structure. The Raman spectrum characterizes molecules uniquely. Since Raman spectrometry relies on bond polarizability and is able to measure low frequencies, it is sensitive to crystal lattice vibrations that provide information about polymorphism. This allows using Raman spectroscopy with great efficiency in the study of crystallization and other complex processes for which FT-IR spectroscopy is less informative. However, when choosing Raman spectroscopy as the method of analysis, it is necessary to take into account the propensity of a particular sample to fluorescence. Raman scattering is a weak effect, and fluorescence can muffle the signal, with making it difficult to obtain high-quality data. The solution to this problem is to use an excitation source with a longer wavelength.

Although IR and Raman spectroscopy are interchangeable in many cases and complement each other well, there are differences that should be considered when choosing the method. Most molecules with symmetry manifest themselves in both the IR and Raman spectra. A special case is represented by molecules with an inversion center, the presence of which leads to mutually exclusive Raman and IR bands, so the bond will be active only in one of the spectra. There is a general rule: functional groups with strong changes in the dipole moment are clearly visible in the IR spectrum, whereas functional groups with weak changes or with a high degree of symmetry are better visible in Raman spectra.

The ReactRaman systems, which are devices with a universal design and best-in-class characteristics, can be used for online monitoring. The spectrometer has a small size, lightweight and high temperature stability, which allows performing accurate measurements in different conditions. In addition, the ReactRaman system can be easily combined with FT-IR, particle characterization system and automated laboratory reactors for study in detail and control of the process.

2. Experimental part

2.1. Reagents

4,4'-methylendiphenyldiamine (MDA), triphosgene (BTC), chlorobenzene (MCB).

2.2. Equipment

EasySampler 1210 Mettler Toledo Sampler; FT-IR spectrometer ReactIR 700 SN: B943477161;
Settings used:

1. Detector: TEMCT; Apodization: Norton-Beer Medium; Probe: DiComp (Diamond); SN: B946602782; Interface: AgX 9.5 mm x 1.5 m Fiber (Silver Halide); Sampling: 1950 to 750 cm^{-1}; Resolution: 4; Scan option: AutoSelect; Gain: Low);
2. Detector: TEMCT; Apodization: Norton-Beer Medium; Probe: DiComp (Diamond); SN: B946602782; Interface: AgX 9.5mm x 1.5m Fiber (Silver Halide); Sampling: 3000 to 650 cm^{-1}; Resolution: 8; Scan option: AutoSelect; Gain: Medium);
3. Detector: TEMCT; Apodization: Norton-Beer Medium; Probe: DiComp (Diamond); SN: B946602782; Interface: AgX 9.5mm x 1.5m Fiber (Silver Halide); Sampling: 3000 to 650 cm^{-1}; Resolution: 8; Scan option: AutoSelect; Gain: Low);

- Raman spectrometer ReactRaman0213 (Serial Number: 10000213, Sampling from 3200 to 100 cm^{-1}; Probe Type: Fiber BallProbe®, dia: 9.5 mm, Probe SN: 0100379; Laser Power: 100 mW, Scans: 22, Exposure Time: .5 sec); Software: iC IR Mettler Toledo and iC Raman Mettler Toledo.

2.3. The procedure of kinetic measurements

There were five experiments with different temperature conditions and concentrations. When using only the FT-IR spectrometer (Table 1, №1), the synthesis unit was a three-necked kinetic cell

with a thermostatically controlled jacket (coolant – PMS-10). The central neck was equipped with a mechanical stirring device (stirring speed 250 rpm); antlered forstoss was placed in the lateral neck with an automatic sampler EasySampler 1210 in the direct bend of the forstoss and backflow condenser in the curved bend. The iC IR probe was placed into the second lateral neck.

When using both the FT-IR and Raman spectrometers (Table 1, №2-5), the unit was a three-necked kinetic cell with a thermostatically controlled jacket (coolant – PMS-10) and a magnetic stirrer bar (stirring speed 500 rpm). The iC Raman probe was placed into the central neck, and antlered forstoss was equipped in the lateral neck with an automatic sampler EasySampler 1210 in the direct bend of the forstoss and backflow condenser in the curved one. The iC IR probe was placed into the second lateral neck.

After assembling the unit, chlorobenzene (MCB) and triphosgene (BTC) were placed into the kinetic cell and mixed until completely dissolved. The reaction mass was heated to the initial temperature (T_{in}), and the blank sample was taken. Then MDA was added, and the timer started. Samples were taken using an automatic sampler with an interval of 2, 5, 8, 11, 15, 20, 30 min from the moment of adding MDA. Then, the temperature of the reaction mixture was raised stepwise to the final temperature (T_{fin}), with controlling the reaction passing with IR- or both IR- and Raman spectrometers.

Table 1. MDI synthesis conditions

№	MDA quantity, mol	Mass ratio reactants MDA:BTC	T_{in}, oC	T_{fin}, oC	MDA concentration, M	Spectra	FT-IR spectrometer settings
1	0.0099	1:3	60	90	0.0396	FT-IR	2
2	0.0127	1:3	20	125	0.0635	FT-IR + Raman	2
3	0.011	1:10	40	129	0.055	FT-IR + Raman	2
4	0.023	1:3	30	140	0.115	FT-IR + Raman	3
5	0.023	1:3	30	140	0.23	FT-IR + Raman	1

2.4. Sample preparation and analysis

Using the EasySampler 1210 Mettler Toledo sampler, 20 µl of the reaction mixture was taken, the stop reagent (dipropylamine in acetonitrile 1:10 v/v) was added, and the mixture was diluted 110 µl of a 5% dimethyl sulfoxide (DMSO) solution in acetonitrile. Samples were analyzed by reversed-phase high performance liquid chromatography (HPLC). Chromatographic conditions are presented in Table 2.

Table 2. Chromatographic conditions

№	Name	Characteristic
1	Chromatographic column	Luna Omega PS C18. 150 x 4.6 mm, 3 µm, 100 Å*
2	Mobile phase	Purified water - acetonitrile in a ratio of 40 - 60
3	Chromatography mode	Isocratic
4	Detector wavelength	254 nm
7	Mobile phase flow rate	1,0 ml/min
8	Injected sample volume	20 µl**

** -other columns may be used, provided the analytical system suitability criteria are met.*
*** correction of the volume of the injected sample is allowed in the case of working with diluted or concentrated samples.*

The retention times of the determined components under the conditions described above are shown in Table 3. The determination of the calibration coefficients (extinction coefficients) was carried out in each individual case according to the chromatograms of standard solutions.

Table 3. Approximate retention times of the determined components

№	Name	Estimated retention time, min
1	Dimethyl sulfoxide	3.0
2	MDA	3.5
3	Chlorobenzene	11.1
4	MDI	20.6

2.5. The procedure of online monitoring of MDI synthesis during the reaction with online IR-spectroscopy

Device: ReactIR 700 (SN: B943477161; Detector: TEMCT; Apodization: Norton-Beer Medium; Probe: DiComp (Diamond); SN: B946602782; Interface: AgX 9.5 mm x 1.5 m Fiber (Silver Halide); Sampling: 1950 to 750 cm-1; Resolution: 4; Scan option: AutoSelect; Gain: Low). Software: iC IR 7.1

The ReactIR 700 device was connected, and the IR probe was installed in the sampling hole, so that there was no contact with the reaction mass at the initial moment. After running the iC IR 7.1 program, all necessary service manipulations with the device was performed before starting work. These manipulations included warming up the device to a temperature above 30℃, wiping the probe in the base to eliminate all impurities from the tip of the probe. Then the environment background was collected (Figure 2).

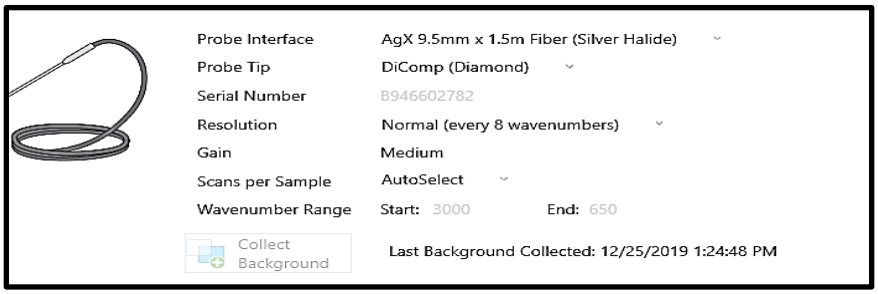


Figure 2. The IC IR 7.1 program interface, collecting environmental background in the reactor

The program automatically subtracts this recorded background from the final spectra, thereby reducing the noise of the received data. After recording the background, the IR probe was immersed into the reaction mass and the "Quick start" mode was started. In the "Quick start" mode, the reaction time can be set from 4 to 16 hours, the optimal time is 8 hours with the 1 min interval between scans. The process starts by clicking the Play button. 5 minutes after the start of the process before adding all the initial components, the spectrum must be recorded, since this spectrum should be used as a solvent spectrum for subtracting from the IR spectrum of the reaction mixture. That allows determining the trends of the formed substances more accurately.

After recording the solvent spectrum, the process started by setting the required temperature and adding reagents step by step. Then, after adding the last reagent, the process of searching for changes in peaks intensity over time was done in the Find Trends tab, with characterizing each individual molecule by the peaks intensity. In this method, the wavelengths should be set manually (table 4). These wavelengths allow tracking intermediates and final products online.

Table 4. Characteristic absorption wavelengths for online monitoring of MDI synthesis with IR spectroscopy

№	Substance name	IR absorption wavelengths
1	Methylendiphenyldiisocyanate (MDI)	1384 cm^{-1}; 1528 cm^{-1} 1022 cm^{-1}; 1230 cm^{-1} 1498 cm^{-1}; 1525 cm^{-1} 1143 ccm^{-1}; 1108 cm^{-1}
2	4,4'-Methylendiphenyldiamine (MDA)	1552 cm^{-1}
3	(Methylenebis(4,1-phenylene))dicarbamic chloride (MDC)	1076 cm^{-1}
4	Triphosgene (BTC)	1180 cm^{-1}
5	Phosgene	1804 cm^{-1}; 839 cm^{-1}

3. Results discussion

The study was performed in three stages:

1. Determination of individual IR spectra of MDA and MDI in monochlorobenzene as a solvent;
2. Study of the reaction of MDI synthesis using online IR and online Raman spectrometers;

3. Development of method for online control of MDI formation during the reaction using Raman and IR spectrometry.

IR spectra were taken for 0.1%, 0.2%, 0.5% and 1% solutions of the reagents in chlorobenzene using the FT-IR spectrometer ReactIR 700 SN: B943477161 (Detector: TEMCT; Apodization: Norton-Beer Medium; Probe: DiComp (Diamond); SN: B946602782; Interface: AgX 9.5 mm x 1.5 m Fiber (Silver Halide); Sampling: 3000 to 650 cm^{-1}; Resolution: 8; Scans: 128). IR spectra for 1% chlorobenzene solutions of individual substances (participants of the chemical reaction) are shown in Figure 3.

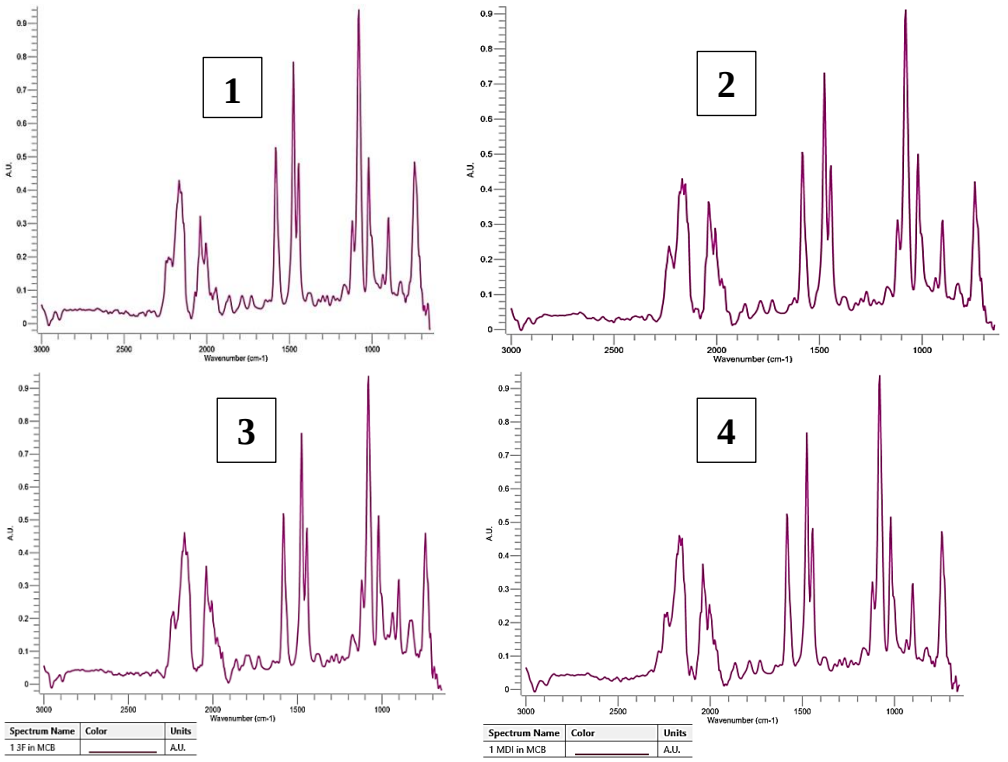
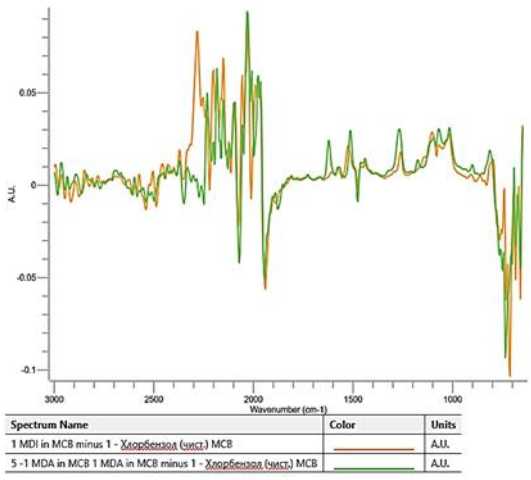


Figure 3. IR spectra of monochlorobenzene (1), 1% MDA in chlorobenzene (2), 1% triphosgene in chlorobenzene (3), 1% MDI in chlorobenzene (4)

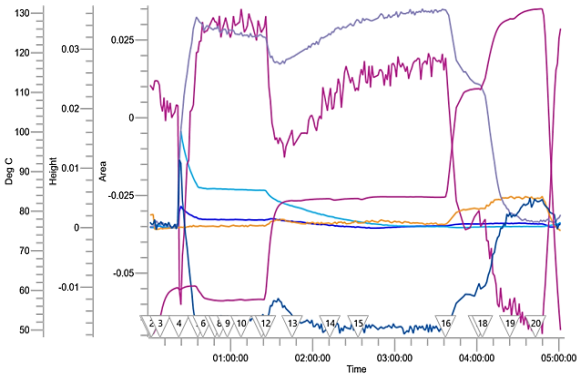


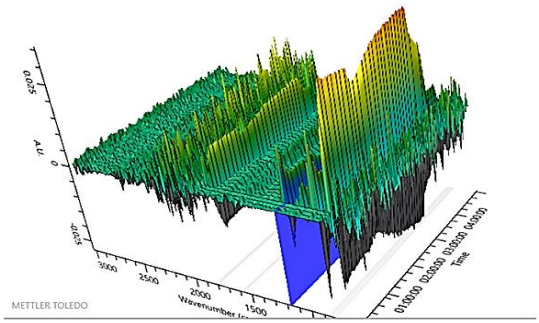
Identification of MDI and MDA can be accomplished by subtracting chlorobenzene spectra from solutions spectra and determining characteristic wavelengths for MDA and MDI (Figure 4). These wavelengths can be used for online IR spectrometry.

Figure 4. Subtraction of chlorobenzene spectra from spectra of MDA and MDI in chlorobenzene solutions

To study the reaction of MDI formation using online IR spectrometers and online Raman spectrometers, five experiments were performed with different temperature conditions and concentrations. During online IR and Raman spectroscopy, samples were taken and analyzed by HPLC after sample preparation.

At the initial stage, the reaction was performed with a threefold mass excess of triphosgene relative to MDA. The reaction temperature range was 60-90℃. The reaction duration was 4 hours, with monitoring trends using an IR spectrometer. The online results of IR spectroscopy and 3D surface (change in peak intensity and time as parameters) for experiment 1 are shown in Figure 5.



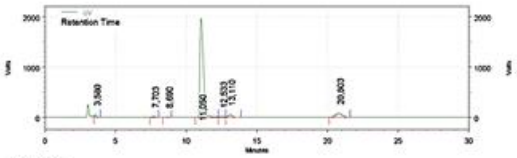


Trend	Color	Units
Peak at 1081 cm-1		Height
Peak at 1179 cm-1		Height
Peak at 1807 cm-1		Area
Peak at 1484 cm-1		Height
Peak at 850 cm-1		Height
Peak at 758 cm-1 1		Height
Probe Temp		Deg C

Figure 5. Online IR spectrometry of experiment 1 (left) and 3D surface (change in wavelength intensity over time) of online IR spectrometry with solvent spectra subtraction (right)

The data of HPLC analysis confirmed the formation of MDI. However, they demonstrate that due to the formation of a large number of stable intermediate products, such as derivatives of carbamoyl chloride by text under the code (MDC), there is a slow expenditure of MDA. HPLC data for the 1st (start of the reaction), 5th (11 min from the start of the reaction), 10th (1h 34 min from the start of the reaction) and the final 14th (4h 4 min from the start of the reaction) specimens are shown in Figure 6.

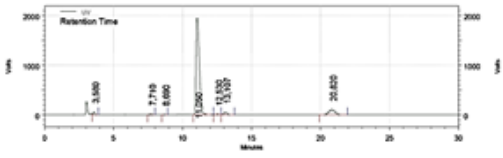
Sample 1



UV Results

Retention Time	Area	Area %	Height	Height %
3,580	1695483	1,14	202662	2,35
7,703	531562	0,36	37629	0,44
8,690	197813	0,13	15370	0,18
11,050	132107362	88,65	7824745	90,62
12,533	812987	0,55	41632	0,48
13,110	3569835	2,40	202335	2,34
20,803	10099305	6,78	310572	3,60
Totals	149014347	100,00	8634945	100,00

Sample 5

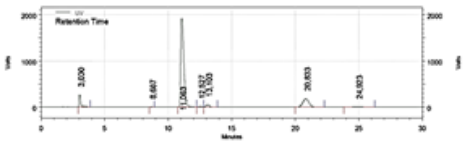


UV Results

Retention Time	Area	Area %	Height	Height %
3,580	2027502	1,35	243531	2,79
7,710	669284	0,44	47495	0,54
8,690	153012	0,10	13981	0,16
11,050	130243133	86,55	7785127	89,15
12,530	569556	0,38	33935	0,39
13,107	3384385	2,25	197309	2,26
20,820	13443369	8,93	411709	4,71
Totals	150490241	100,00	8733087	100,00

Figure 6. HPLC data for 1,5 specimens for experiment 1

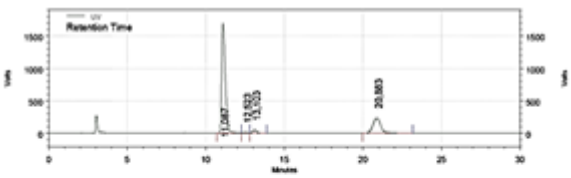
Sample 10



UV Results

Retention Time	Area	Area %	Height	Height %
3,030	8648863	5,16	1051125	10,80
8,687	144260	0,09	13618	0,14
11,063	128885844	76,96	7682348	78,96
12,527	730761	0,44	38756	0,40
13,103	3530748	2,11	200450	2,06
20,833	23877235	14,26	717497	7,37
24,923	1646583	0,98	25886	0,27
Totals	167464294	100,00	9729680	100,00

Sample 14

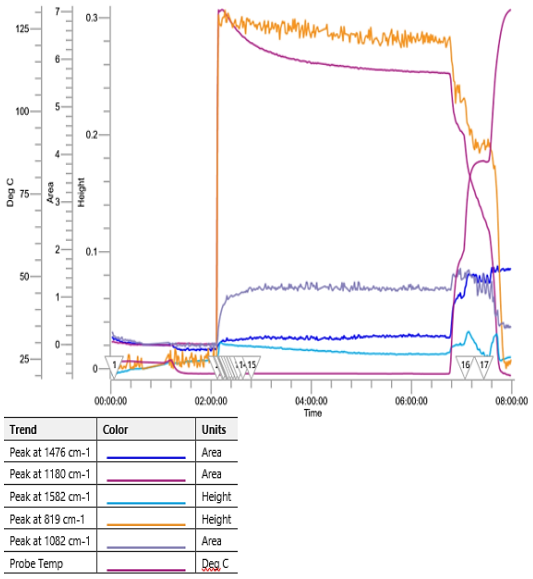


UV Results

Retention Time	Area	Area %	Height	Height %
11,087	109981786	75,39	6772546	85,44
12,523	750556	0,51	37988	0,48
13,103	3275744	2,25	187164	2,36
20,883	31871315	21,85	929035	11,72
Totals	145879401	100,00	7926733	100,00

Figure 6. HPLC data for 10 and 14th specimens for experiment 1

At the next stage, the temperature was increased stepwise from 20 to 125℃. The ratio of reagents was unchanged. The reaction was controlled by IR and Raman spectrometers. The reaction time was 5 h 42 min. The results of online IR spectrometry and 3D surface for online IR spectrometry for experiment 2 are shown in Figure 7.



Trend	Color	Units
Peak at 1476 cm-1		Area
Peak at 1180 cm-1		Area
Peak at 1582 cm-1		Height
Peak at 819 cm-1		Height
Peak at 1082 cm-1		Area
Probe Temp		Deg C

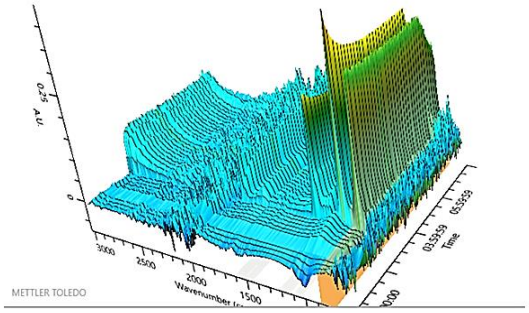
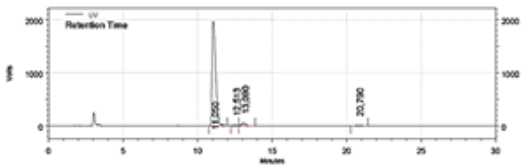


Figure 7. Online IR spectrometry of experiment 2 (left) and 3D surface (change in wavelength intensity over time) of online IR spectrometry (right)

Experiment 2 demonstrates a larger accumulation of the final product (MDI). However, along with MDI, intermediate products were still present in the final reaction mass. HPLC analysis confirms this observation.

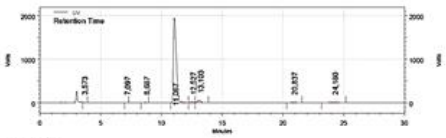
Sample 1



UV Results

Retention Time	Area	Area %	Height	Height %
11,050	133757923	96,18	7868954	96,62
12,513	813016	0,58	41563	0,51
13,090	3607396	2,59	202276	2,48
20,790	888867	0,64	31409	0,39
Totals	139067202	100,00	8144202	100,00

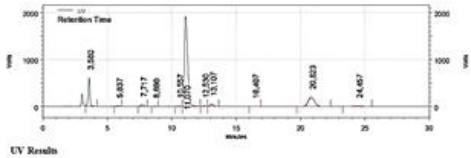
Sample 5



UV Results

Retention Time	Area	Area %	Height	Height %
3,573	155919	0,11	17985	0,22
7,097	35977	0,03	4020	0,05
8,687	224730	0,16	16489	0,20
11,067	133523826	94,86	7791170	95,85
12,527	773863	0,55	39810	0,49
13,103	3604418	2,56	201465	2,48
20,837	965244	0,69	33448	0,41
24,180	1473050	1,05	24120	0,30
Totals	140757027	100,00	8128507	100,00

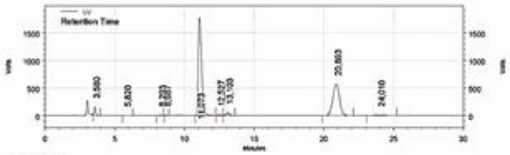
Sample 10



UV Results

Retention Time	Area	Area %	Height	Height %
3,580	21271730	11,43	2434850	21,44
5,837	667188	0,36	48327	0,43
7,717	2027118	1,09	139925	1,23
8,690	162672	0,09	14417	0,13
10,557	210652	0,11	14994	0,13
11,070	129794977	69,71	7667139	67,50
12,530	429019	0,23	28967	0,26
13,107	3247086	1,74	193271	1,70
16,407	229105	0,12	10276	0,09
20,823	26530390	14,25	781305	6,88
24,437	1614382	0,87	25186	0,22
Totals	186184319	100,00	11358657	100,00

Sample 12



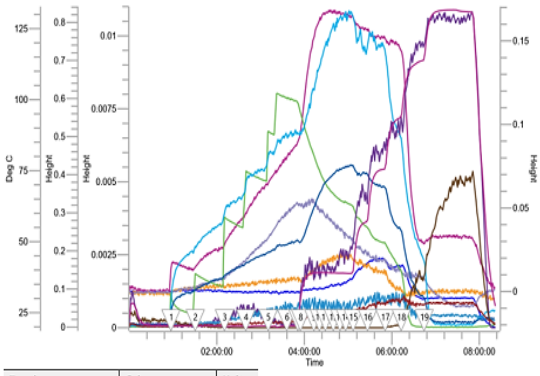
UV Results

Retention Time	Area	Area %	Height	Height %
3,580	5210858	2,58	618161	6,06
5,820	75088	0,04	4400	0,04
8,293	187542	0,09	13825	0,14
8,687	104792	0,05	10777	0,11
11,073	117125514	58,01	7059643	69,22
12,527	387592	0,19	26442	0,26
13,103	3004162	1,49	179616	1,76
20,893	74319169	36,81	2261851	22,18
24,010	1489535	0,74	24161	0,24
Totals	201904252	100,00	10198876	100,00

Figure 8. HPLC data for 1,5,10 and 12th specimens for experiment 2

Chromatograms for the 1st (start of the reaction), 5th (15 min from the start of the reaction), 10th (4 h 42 min from the start of the reaction) and the final 12th (5 h 42 min from the start of the reaction) samples are shown in Figure 8.

The next step was an attempt to increase the excess of triphosgene significantly (to 10 times). The reaction temperature range was slightly changed to 40-129℃. Triphosgene and MDA were added in portions of 10, 20, 30, 40, 60, 80, 100 mass % of the total amount of BTC and MDA, with controlling the addition using iC IR and iC Raman. The reaction time was 9 hours and 15 minutes. The results of online spectroscopy and 3D surface (change in peak intensity and time as parameters) for experiment 3 are shown in Figure 9 (for IR spectroscopy) and figure 10 (for Raman spectroscopy).



Trend	Color	Units
MDX Peak at 1576 cm-1		Height
Peak at 1076 cm-1		Height
Peak at 1328 cm-1		Height
Peak at 1377 cm-1		Height
3F_Peak at 1180 cm-1		Height
1F_Peak at 839 cm-1		Height
1F_Peak at 1804 cm-1		Height
Peak at 1552 cm-1		Height
Peak at 1179 cm-1		Height
MDI Peak at 1384 cm-1		Height
Peak at 1022 cm-1		Height
Probe Temp		Deg C

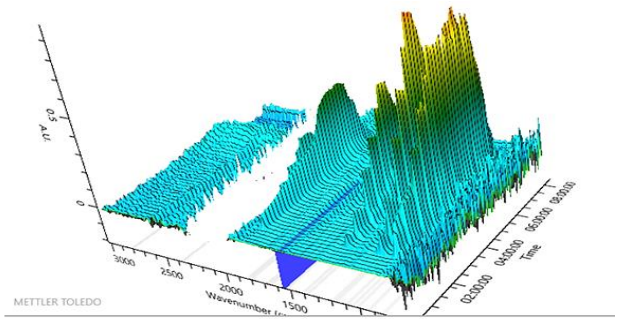
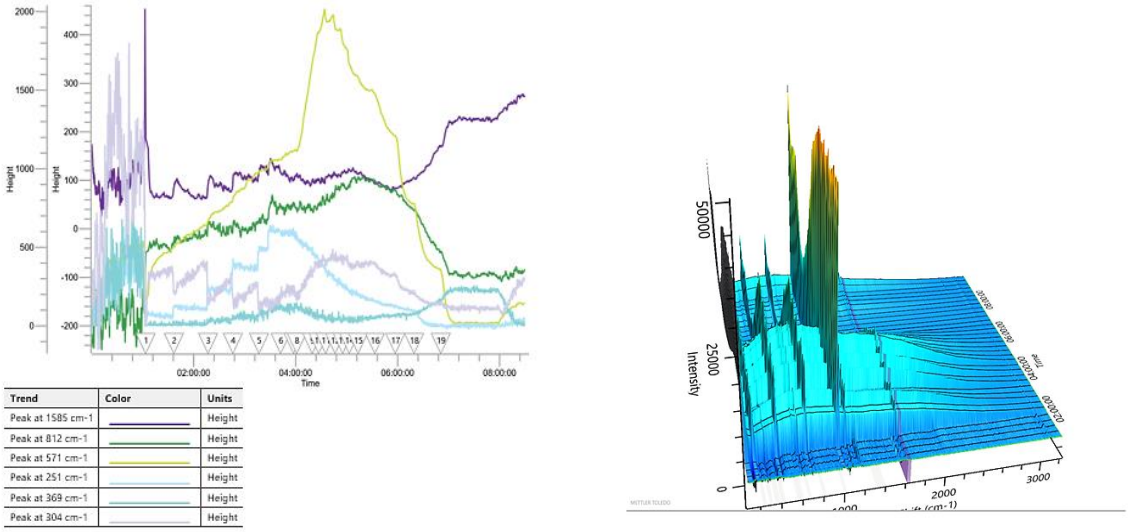


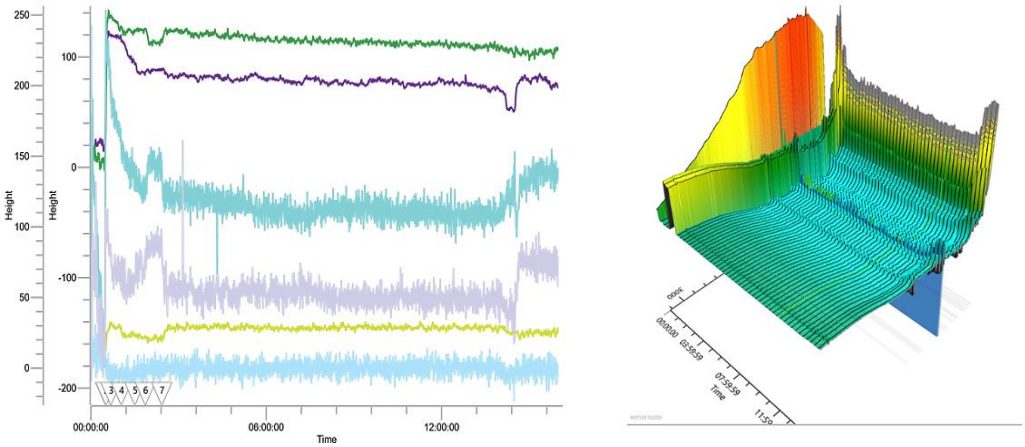
Figure 9. Online IR spectrometry of experiment 3 (left) and 3D surface of online IR spectrometry (right)



Trend	Color	Units
Peak at 1585 cm-1		Height
Peak at 812 cm-1		Height
Peak at 571 cm-1		Height
Peak at 251 cm-1		Height
Peak at 369 cm-1		Height
Peak at 304 cm-1		Height

Figure 10. Online Raman spectroscopy of experiment 3 (left) and 3D surface of online Raman spectroscopy (right)

The Raman spectrometer was unable to collect a sufficient amount of backscattering data to the sensor device was able to show significant differences in the change of intensity over time. In the next experiment, we used the original ratio of reagents, but amounts were increased in order to improve result. The results of online Raman spectroscopy and 3D surface (change in peak intensity and time as a parameter) for experiment 4 are shown in Figure 11.



Trend	Color	Units
Peak at 1585 cm-1		Height
Peak at 812 cm-1		Height
Peak at 571 cm-1		Height
Peak at 251 cm-1		Height
Peak at 369 cm-1		Height
Peak at 304 cm-1		Height

Figure 11. Online Raman spectroscopy of experiment 4 (left) and 3D surface of online Raman spectroscopy (right)

Due to the fact that it is difficult to separate the MDI peak from other peaks (the resolution was not enough), it was decided to add 5 grams of a premade MDI to the reaction mixture in order to "highlight" the wavelengths that characterize MDI. This effect should be observed as

the intensity of peaks increasing. The results of online Raman spectroscopy and 3D surface online Raman spectroscopy after adding 5 grams of premade MDI are shown in Figure 12.

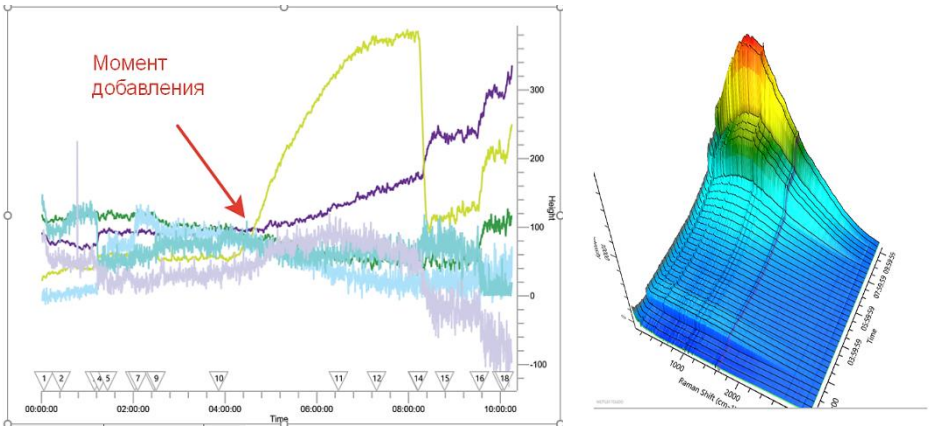


Figure 12. Online Raman spectroscopy (left) and 3D surface of online Raman spectroscopy (right) for experiment 4 after 5 grams of premade MDI addition

It can be noticed that it is not possible to "highlight" the wavelengths that characterize the MDI after the premade MDI addition. The intensity of peaks increases along the entire front of the Raman shift wavelengths. This observation can be explained by the fact that the resolution of the Raman spectrometer is insufficient and/or it is necessary to change the laser power from 100 mW to a higher value, for example, 300 mW. In this case, a fundamentally different form of Raman spectra will be observed.

The final experiment (№5) was performed with large amounts and high temperature. The result of Raman spectroscopy of experiment 5 also did not show satisfactory results. All peaks increase in proportion to the temperature rising, what makes it impossible to identify the characteristic Raman shift of reaction products and intermediates with high accuracy (Figure 13).

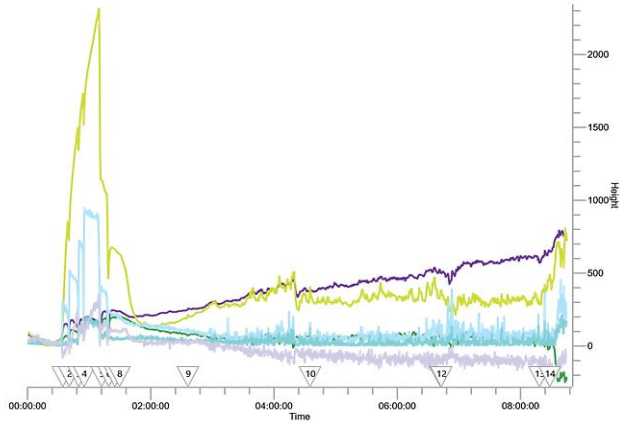
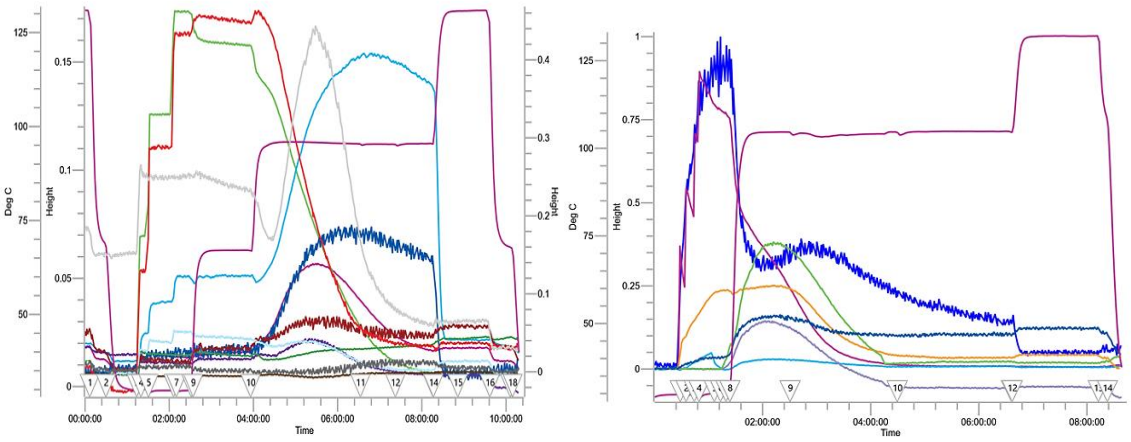


Figure 13. Online Raman spectroscopy of experiment 5

Experiments 4 and 5 demonstrated that sensitivity of the device and laser radiation equal to 100 mW does not allow identifying the characteristic peaks for the reaction products and intermediates with a high accuracy. However, the online IR spectroscopy demonstrated sufitient results in determining both reaction products and intermediates (Figure 14).



Trend	Color	Units
MDX Peak at 1076 cm-1		Height
3F_Peak at 1180 cm-1		Height
1F_Peak at 839 cm-1		Height
1F_Peak at 1804 cm-1		Height
MDA/MDX Peak at 1552 cm-1		Height
MDI? Peak at 1528 cm-1		Height
MDI Peak at 1384 cm-1		Height
Peak at 1022 cm-1		Height
Peak at 1230 cm-1		Height
MDI? Peak at 1498 cm-1		Height
Probe Temp		Deg C
Peak at 1619 cm-1		Height
Peak at 1502 cm-1		Height

Figure 14. Online IR spectrometry of experiment 4 (left) and 5 (right)

During experiment 4 (after adding 5 grams of premade MDI), the characteristic absorption wavelengths for MDI to control its accumulation in the reaction of MDA and triphosgene in a chlorobenzene medium, on the ReactIR 700 equipment (SN: B943477161; Detector: TEMCT; Apodization: Norton-Beer Medium; Probe: DiComp (Diamond); SN: B946602782; Interface: AgX 9.5 mm x 1.5 m fiber (silver halide); sampling: 1950 to 750 cm^{-1}; resolution: 4; scan option: Autoselect; Gain: Low) were found. These wavelengths are presented in Figure 15. The absorption wavelength of 1384 cm^{-1} for MDI intersects with the IR spectra of other reagents in the minimal degree.

Zero_Peak at 1528 cm-1		Height
MDI Peak at 1384 cm-1		Height
Peak at 1022 cm-1		Height
Peak at 1230 cm-1		Height
Peak at 1498 cm-1		Height
Peak at 1525 cm-1		Height
Peak at 1143 cm-1		Height
Peak at 1108 cm-1		Height

Figure 15. IR absorption peaks of MDI in MCB that overlap with the absorption peaks of other substances minimally

Absorption wavelengths for monitoring other reagents in online IR spectroscopy are also found (Table 3).

4. Conclusion

Based on the results of the research, the following results were obtained:

- the individual IR spectra of MDA and MDI in monochlorobenzene were established;
- kinetic studies of the MDI synthesis reaction using the online IR and online Raman spectrometers were performed to identify the possibility of their use;
- the method for online control of the MDI synthesis reaction using IR spectrometry was developed.

The development of a method for online control of the MDI synthesis reaction using Raman spectrometry was not successful due to the low resolution of the equipment and the selected laser power. The developed method using IR spectrometry allows applying this method to control the reaction process in online mode for the pilot plant.

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