

Ionic liquids – the path to the first industrial application

DARKO LOVREC

Abstract When using hydraulic fluids, users rarely ask themselves how the development of the hydraulic fluid they use in their hydraulic device has gone. Perhaps only curious users want to know the approximate composition of the newer, better hydraulic fluid, compared to the fluid of the previous generation. Rarely, however, do they know the developmental pathway of the new fluid. Even in the case of minor changes in the chemical composition of the fluid, e. g. a newer package of additives for mineral oils, or other base oil, requires lengthy fluid testing. First, in the manufacturer's laboratories, and then in the industrial environment. In the case of a completely new type of hydraulic fluid, the development path is much longer. The paper presents the behind-the-scenes development of a completely new type of hydraulic fluid - ionic liquid, from learning about the liquid itself all the way to industrial application.

keywords: • hydraulic fluids • ionic liquids • selecting • testing • application •

CORRESPONDENCE ADDRESS: Darko Lovrec, University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, Slovenia, e-mail: darko.lovrec@um.si.

DOI <https://doi.org/10.18690/978-961-286-513-9.17>
Dostopno na: <http://press.um.si>.

ISBN 978-961-286-513-9

1 Introduction

The development of hydraulic fluid is a long-lasting process. Before the fluid is suitable for use in an industrial environment, a lot of targeted testing is needed, first in a laboratory environment, and then in an industrial environment, after which the process is usually repeated based on users' feedbacks. If the hydraulic fluid has to meet specific operating requirements, the path is even more difficult. In the case of a completely new type of hydraulic fluid, the development is even more difficult, associated with high costs, lengthy and extensive testing and incomparably more unknowns than in the case of "adaptation" of an already known fluid.

We encountered this problem in the development of a completely new type of hydraulic fluid - Ionic Liquid (IL), which would be suitable for use in hydraulic devices. Not only that, but such IL, which would have the properties provided by different types of hydraulic fluids: Nonflammable, environmentally friendly, with good lubricating properties, low temperature dependence, low vapour pressure and others. In addition, when changing the fluid, the user would not need to pay special attention to the compatibility of the fluid with the materials used in the hydraulic components.

The paper provides an insight into our own experience in the development of Ionic Liquids which would be suitable for use in modern hydraulic systems. The entire development path, which has lasted for more than a decade, is presented, divided into individual phases or stages of development. These phases are: learning about the matter and assessing their suitability, finding suitable project partners, selecting suitable candidates, laboratory tests of individual properties, endurance testing on a dedicated test device and, finally, an industrial application.

2 Stage 1: Learning about the material - Ionic Liquids

Ionic Liquids are usually, and very simply, called liquid salts. The application of high temperature molten salts in ancient China dates back to the 2nd century B.C., and is even evident during the Shang Dynasty (16th to 11th centuries B.C.). These molten salts, based on alkali nitrates and chromates, were used for the surface modification of bronze weapons, in order to make them harder and corrosion protected. Ionic Liquids are defined as molten salts with a melting temperature

of 100 °C or lower [1], [2] in the liquid state, a large number of them even being liquid at room temperature, and then being called “room temperature molten salts”. Compared to conventional molten salts they show some characteristic differences, as presented in Table 1.

Table 1: Comparison of "molten salts" and "Ionic Liquids" [1]

“Molten Salts”	“Ionic Liquids”
High melting points: ~200 °C to ~1500 °C	Melting point ≤100 °C down to approx. -60 °C
Aggressive chemical reactivity, high corrosion	Mild chemical reactivity, low corrosion
Considerable vapour pressure	Virtually no vapour pressure
Inorganic cations and anions	Organic cations
Strongly coordinating ions	Weakly coordinating ions

In 1888 *Gabriel* and *Weiner* published details of the organic salt ethanolanmonium nitrate ($\text{HOC}_2\text{H}_4\text{NH}_3^+\text{NO}_3^-$) with a melting point of 52 to 55 °C [3]. In 1914, the field of true room temperature Ionic Liquids started off with the fateful discovery of ethylammonium nitrate ($\text{EtNH}_3^+\text{NO}_3^-$), having a melting point of only 12 °C. Ionic Liquids have evolved rapidly to the present day, with the structure and properties of IL adapted to the field of application. Ionic Liquids typically consist of an organic cation and an inorganic or organic anion (R denoting an alkyl or aromatic rest, optionally functionalised).

Ionic Liquids with a melting point at ambient temperature, which is suitable for use as a liquid lubricant and as a hydraulic fluid, consist of extensive and asymmetric organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, 1-methyl-1-alkylpyrrolidinium or ammonium ions. Many anions are in use, from simple halides that lower high melting points, to inorganic anions such as tetrafluoroborates and hexafluorophosphates, and to large organic anions such as bis (trifluorosulfonyl) amides, triflates or tosylates [4]. An example is shown in Figure 1. For non-chemists, Ionic Liquids are complex chemical structures and their names are also complex too. Therefore, often when we talk about the type and structure of Ionic Liquid, we use an abbreviation, such as, e. g., for the often-mentioned Ionic Liquid EMIM EtSO₄ >: 1-Ethyl-3-methylimidazolium ethyl sulfate.

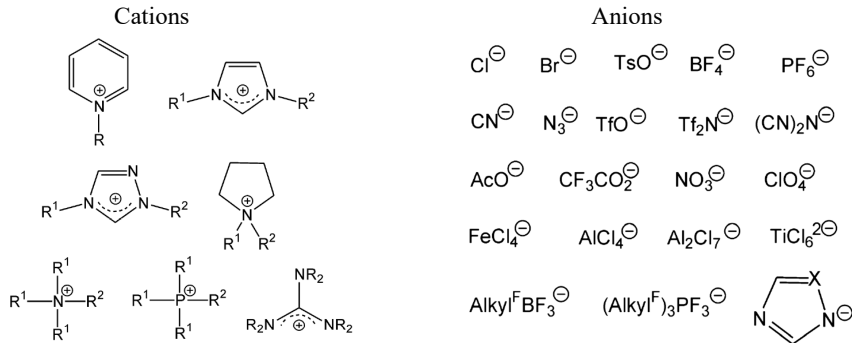


Figure 1: Various cations and anions in Ionic Liquids [3].

Since the 1990's thousands of review papers and dozens of books have been published describing the amazing physical and chemical properties of Ionic Liquids, (see the references given in [1]). The most outstanding properties of Ionic Liquids reported in different publications are the following:

- Excellent lubrication properties,
- Very low melting points (100 °C down to – 60 °C)
- Virtually no vapour pressure (no pollution via the gas phase),
- No boiling point,
- Non flammable (below the thermal decomposition point),
- Excellent thermal long term stability up to 300 °C and more,
- Very large liquidus range up to 400 °C,
- Unusual solvation properties (e. g. amphiphilicity),
- Frequently and improved catalytic performance,
- Small friction coefficients, good lubrication properties,
- Electrical conductivity (typically 100 to 10000 $\mu\text{S}/\text{cm}$ at 20 °C),
- Bacteriocide to bacteriostatic properties, no biofouling,
- Tunable by structure variation of cations, anions and by changing their combination: Millions - virtually unlimited – structures, etc.

All of these highlighted excellent properties of a particular type of ionic fluid were reason enough to stimulate our interest in the possible use of ionic fluid as a hydraulic fluid. A fluid that would have all of the aforementioned excellent listed properties, would solve a huge number of problems arising from the use of the current hydraulic fluids.

3 Stage 2: Goal setting – project HOPE

Enthusiastic and encouraged, based on the information gathered, we started looking for partners for a project in which we could fully select, test and also use suitable fluids in hydraulic systems. Given this, a partner would certainly need to be a very experienced manufacturer of Ionic Liquids, a company that had experience in the production and testing of conventional hydraulic fluids and was adequately equipped for these tasks, and also a company that would be willing to approach the development in terms of hydraulic components, and, of course, a Research Institution that would conduct and direct the research, perform certain special tests, connect all partners in the project and, based on the research results, look for suitable applications for the practical use of Ionic Liquids.

The partners in this project came from three different countries: Austria, Germany and Slovenia: The HAWE company – a manufacturer of hydraulic components and systems, the OLMMA company – the leading Slovenian manufacturer of lubricants, the Proionic company from Graz/Austria, one of the leading global manufacturers of ILs, and the University of Maribor, where we carried out the majority of the research and connected all the partners, in cooperation with the Technical University of Graz/Austria and other partners from the industry e. g. Bogadi, a specialist in the production of seals, Mettop, a specialist in the production of machines and devices for the steel industry.

The main goal of project HOPE was to check the suitabilities of the existing ILs for usage within hydraulic systems, and/or to synthesise such ILs, which would have better physical and chemical properties – should be (almost) an ideal hydraulic fluid, which we were already looking for from the first hydraulic presses onwards.

The following main objectives were set in the implementation of the project:

- From a wide range of ILs suitable for technical usage, to find an appropriate IL for use in modern hydraulic systems,
- Determinations of their physical-chemical properties,
- Performing a comparison with today's more commonly used hydraulic fluids: Mineral oil, fire resistant fluids, and biologically rapidly degradable fluid,

- To provide recommendations for the usages of ILs with the best properties within various industrial applications,
- To check the suitability of existing laboratory methods for determining the properties of ILs.

4 Stage 3: Preselection – checking the properties

As already mentioned, ILs consist of an organic cation and an inorganic or organic anion. However, when combined with certain specified cation anions, you will obtain another liquid salt – which, if it does not work by trial and error but intentionally, can be synthesised into a completely new material with entirely new properties. In our case, we are looking for “liquid salts”, which would have the characteristics of a perfect hydraulic fluid.

An important feature of Ionic Liquids is the possibility of adapting these physical-chemical properties through changing the natures of the anions and cations. The number of possible combinations is extremely high, which is why the best Ionic Liquid is supposed to be adapted for different usage: 1.10¹⁸. For this reason, the first objective of the project was, from the almost unlimited possibilities of combinations of ions and cations, with a screening process, to extract those combinations which would be suitable for use as a hydraulic fluid.

Selecting the “best ILs` suitable candidates” for use as hydraulic fluids, the work with ILs, is however, not as uniformly definite as with other conventional lubricants. It is because of their unique properties that Ionic Liquids frequently impose the use of special laboratory equipment.

The majority of laboratory measurements were carried out within the chemical laboratory of the lubricant manufacturer, which has the appropriate equipment, using a wide assortment of analytical methods, out of which many were also applicable for ILs, for example, measurements of viscosity, density, corrosion, Karl Fischer titration, UV/VIS spectroscopy, FTIR spectroscopy, Thermo-Gravimetric Analysis, measurements of lubricating and foaming properties, etc. Some methods, such as the measurement of breakdown voltage, filtration capacity, Stribeck’s curve, and Contact Angle were applied in other proper laboratories.

Test procedures for determining the individual parameters, sample amounts and the equipment used, relate mainly to the usual lubricants, in accordance with the relevant Standard. In addition, the tests of Ionic Liquids (as lubricants), were based on those processes intended particularly for the testing of mineral oil (liquid lubricants), and, as such, served as a starting-point. In our case, we first performed the following standard tests:

- Flash and fire points by the Cleveland Open Cup tester; ASTM D 92,
- Flash-point by the Pensky-Martens Closed Cup Tester; ASTM D 93,
- Determination of density by a densimeter; ISO 12185,
- Kinematic viscosity at 40 °C and 100 °C; ASTM D 445,
- Determination of viscosity index; ASTM D 2270,
- Determination of corrosion within a humid chamber; ISO 6270-2,
- Determination of corrosiveness to copper; ASTM D130,
- Determination of demulsifying properties; ASTM D 1401,
- Determination of foaming in lubricating oils; ASTM D 892,
- Determination of the welding point and wear diameter; IP 239-85,
- Determination of the pour-point; ASTM D 97.

The methods listed so far are used as the standard methods for the determination of physical-chemical properties, particularly of different lubricating oils, and were used as a starting-point for testing the Ionic Liquids' properties.

In addition to the mentioned and used standard tests, special purposeful measurements of physical-chemical properties were also used for testing the Ionic Liquids, as well as comparing fluids:

- Filterability; ISO 13357, and compatibility with filter materials,
- Compatibility with paint coats and with sealing material,
- Compatibility with metals used within hydraulic components,
- Measurement of Stribeck's curve,
- Measurement of compressibility and sound propagation,
- Electric breakdown voltage-IEC 156, IEC 60156,
- Contact Angle and wettability,
- Corrosiveness in open air...

Table 2 shows only a small section of the Data Table obtained during the selection process, and for only some of the tested ILs. Determining the suitability of IL was based first on corrosivity testing, then on lubricating properties. Only those ILs that showed good corrosion protection and good lubricating properties were tested further for other properties [5] to [14].

Table 2: Comparisons between some physical-chemical properties of tested ILs

Property Unit	Viscosity 40°C [mm ² /s]	Viscosity index [I]	Welding point [kg]	Wear diameter [mm]	Corrosion [cycles]
Sample					
Hydrolubric VG 46	47.07	119	130/140	0.58	0 (3 h)
EMIM-EtSO ₄	39.44	168	140/180	1,0	0 (15 min)
EMIM-TFSI	71.89	132	1100/1200	0.68	0 (1.5 h)
10PI 453-1	/	/	/	/	0 (5 h)
10PI 453-2	/	/	/	/	0 (1 h)
10PI 453-3	/	/	/	/	0 (1 h)
10PI 453-4	/	/	/	/	0 (30 min)
10PI462 (EMIM-TFS2)	/	/	360/380	0.83	0 (30 min)
10PI465	/	/	>480	1.07	0 (30 min)
16PI028-5 (TOMA-DBP)	/	/	/	/	0 (30 min)
10PI028-3 (TOMA-HFB)	/	/	/	/	0 (45 min)
16PI062-2 (TOMA-DBP)	59.14	/	160/170	/	0 (4 h)
16PI062-1 (TOMA-HFB)	61.46	/	110/120	/	0 (5 min)
18PI094	49.28	109	120/130	1.04	0 (15 min)
19PI042	193.30	116	300/320	0.63	0 (15 min)
TOMA-DBP+10 % TOM- p	60.29	133	130/140	0.82	0 (2.5 h)
EMIM-SCN+42,3 % TOMP	/	/	>200	/	0 (15 min)
17PI064	102.90	105	180/190	0.49	1
18PI163	47.36	155	150/160	0.38	0 (3.5 h)
17PI045	46.59	155	140/150	0.35	0-1 (>7.5 h)

The process of selecting a suitable IL has shown that certain ILs do indeed have excellent individual material properties, as reported in publications. For their use as a hydraulic fluid, the individual excellent properties of different fluids should apply to the same fluid. However, in most cases, due to one good but another bad property, the specific IL is not suitable for use within hydraulic systems.

5 Stage 4: Endurance tests

After the selection process only with those ILs which showed most of the good properties important for use as a hydraulic fluid, it made sense to proceed the testing with real hydraulic equipment and under real operating conditions.

Endurance tests are the next stage of testing the suitability of an Ionic Liquid. For these purposes, so-called tribological tests are usually used with hydraulic pumps (Vickers-Eaton test, Rexroth test, Denison test, Sundstrand test, Komatsu test, etc.) [15]. Unfortunately, these tests focus only on the pump, and not on other, equally important and active components within the hydraulic system. In addition, most of these tests use pumps with large flow rates and, consequently, a large amount of test quantities needed and, consequently, large test devices. The latter can lead to major test stand damage in the case of an unsuitable tested fluid. In addition, it makes sense to test the characteristics and performance of the new fluid in comparison with a known, commonly used hydraulic fluid, e. g. with mineral hydraulic oil [16], [17].

For the purpose of testing new hydraulic fluids, e. g. Ionic Liquids, a new test device concept has been designed and constructed, appropriate for the combined testing of as many hydraulic components as possible, in the market quality. The testing is carried out under demanding, but still normal operating conditions, and with lower energy consumption. The mentioned tribological endurance pump-tests are limited only to a hydraulic pump. Therefore, it is reasonable to design a different concept of testing for a comprehensive insight. The starting points for the new test device design:

- To determine the suitability of the new fluid under real operating conditions,
- Using a variety of hydraulic components of industrial quality, commonly used within hydraulic systems,
- Take into account the aspect of energy consumption,
- Take into account the scale of the test device,

- Take into account the duration of the test,
- Take into account the cost of testing,
- The possibility of on-line monitoring of all important data,
- At certain intervals, to check the changes in the characteristics of the tested components,
- To use the standard test procedures, where possible,
- The possibility of cost-optimal repetition of the test...

In accordance with the listed requirements, a test device was designed for the integrated testing of the impact of a new hydraulic fluid on all components of the hydraulic system— Figure 2.

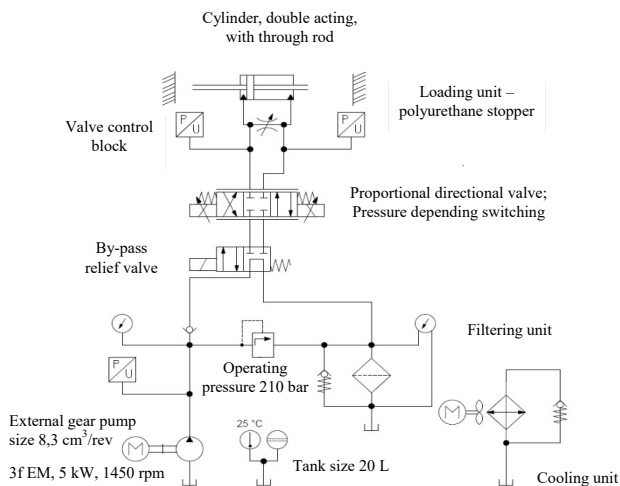


Figure 2: Layout of test device for integral endurance testing of fluid-component interaction [15].

When designing devices for testing of hydraulic fluids along with hydraulic components, there are a few things to consider: Selection of appropriate components, power consumption of the device and type of loading profile. For the testing of an absolutely new fluid, another aspect should be taken into account: Cost effective design.

The test device allows insight into the pump wear, investigation of wear on the vital parts of different valve types (directional spool valve, poppet valve), the impact of the new liquid on a variety of materials used within other hydraulic system components (filter material, paint coat ...), as well as the on-line and off-

line monitoring of the degradation process of the components – Figure 3. Some of these changes are monitored on-line and others off-line after the tests are completed, in total more than 50 different parameters.

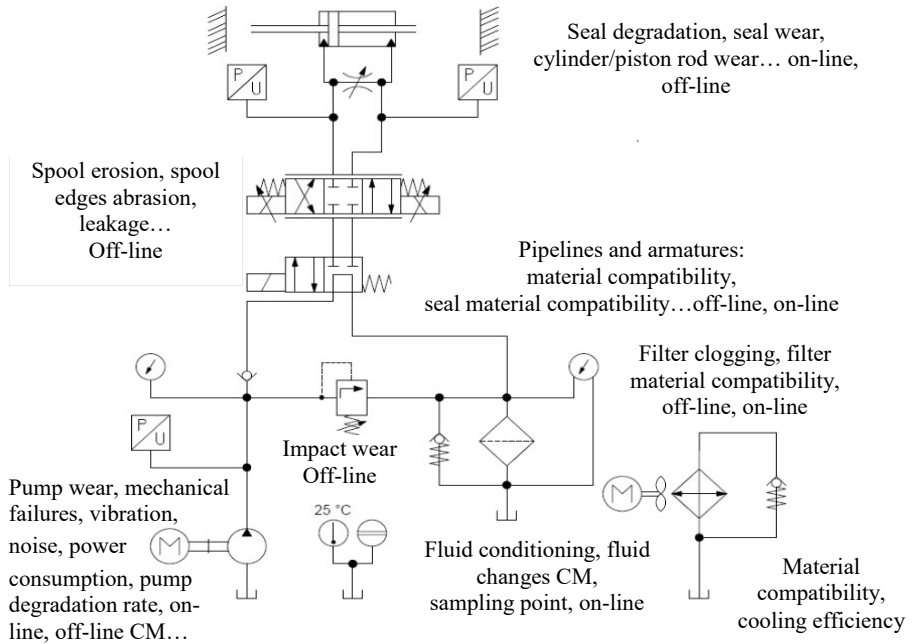


Figure 3: Points of interest and observed parameters [15].

In this way, we got a more comprehensive insight into the effect of the tested new fluid type on the behaviour of the entire hydraulic system during operation, and the effect of the fluid on the degradation of an individual component exposed to real operating conditions (more information available in [15]).

Only after successfully completed endurance tribological tests, which provided a comprehensive insight into the impact of ionic fluid on all components of the hydraulic system, the tested fluid can be used for real industrial application.

6 Stage 5: Industrial application

Ionic Liquids have been used in industrial applications for some time. The first use case dates back to 1936, when IL was used to dissolve and alter cellulose chemically. At present, ILs are used industrially as solvent, catalysts, electrolytes, performance additive, cooling fluid, operating fluid, reagents within different technological processes. [1] However, as a hydraulic fluid, ILs have so far not found their use in the industrial environment (according to available official publications).

The first example of a simple hydraulic lifting device operating on an Ionic Liquid was presented at the international conference Fluid Power 2015. A demonstration device constructed with the industrial hydraulic components used is shown in Figure 4.

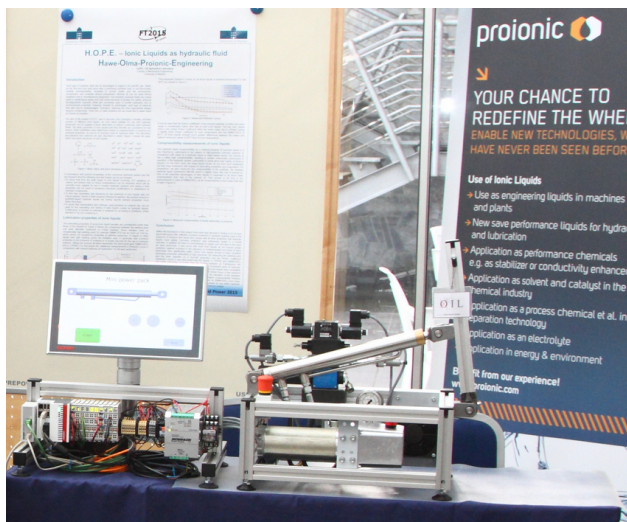


Figure 4: Small lifting device operating on Ionic Liquid

The first major industrial application of a hydraulic system using an Ionic Liquid is the so-called tuyere press, which is used in the metallurgical industry. It is a special application, where no other type of hydraulic fluid can be used. A version was required with the lowest possible weight of the unit with adjustable cylinder speeds and the possibility of integrating additional functions. The main condition, however, was to ensure the fire-safe design of the unit. It is a modern version of the electro-hydraulic axle, where the hydraulic cylinder is controlled

directly by a speed-regulated hydraulic pump with a built-in safety control unit mounted on a linear unit. The advantage of the design is the small amount of Ionic Liquid and a closed system isolated from the specific environment. The appearance of the unit is shown in Figure 5.



Figure 5: The final appearance of the axis during the testing phase.

7 Conclusion

In this paper, the process of developing a new type of potential hydraulic fluid, from the first idea to the first industrial application, is presented on the example of an ionic fluid. The path of development is very long, and usually requires the involvement of experts from various fields, and takes place over at least five stages: From setting target properties, through screening suitable candidates, extensive and varied laboratory tests, and only through long-term laboratory tests of fluid endurance under real operating conditions and components, we arrive at the first application. Based on the feedbacks received, however, certain steps (if necessary) need to be repeated.

References

- [1] Kalb, R. (2015). Ionic liquids – A New Generation of High-Tech Engineering Liquids, A Review. International conference Fluid Power 2015, Maribor. University of Maribor. Proceedings. ISBN 978-961-248-491-0, 49-77.
- [2] Laus, G., Bentivoglio, G., Schottenberger, H., Kahlenberg, V., Kopacka, H., Röder, T., Sixta, H. (2005). Ionic liquids: Current developments, potential and drawbacks for industrial applications, *Lenzinger Berichte*. 84. 71-85.
- [3] Gabriel, S., Weiner, J. (1988). Über einige Abkömmlinge des Propylamins. *Berichte der deutschen chemischen Gesellschaft*, Vol. 21. No. 2. 2669-2679.

- [4] Kambič, M., Lovrec, D. (2011). Hidravlične tekočine prihodnosti: na poti iskanja idealne hidravlične tekočine. Mednarodna konferenca Fluidna tehnika 2011, Maribor. Univerza v Mariboru. 149-162.
- [5] Lovrec, D. (2017). Corrosion protection properties of ionic liquids. ISCAMÉ 2017. 5th International Scientific Conference on Advances in Mechanical Engineering, 017 Debrecen. Hungary. Debrecen: Faculty of Engineering. 306-311.
- [6] Lovrec, D. (2017). Ionic liquid as a novel, high performance hydraulic fluid - selection process. ISCAMÉ 2017, 5th International Scientific Conference on Advances in Mechanical Engineering, Debrecen. Hungary. Debrecen: Faculty of Engineering, 300-305.
- [7] Kambič, M., Kalb, R., Lovrec, D. (2015). Lubrication properties of ionic liquids suitable for use within hydraulic systems. Proceedings of International Conference Fluid Power 2015, University of Maribor. 79-93.
- [8] Lovrec, D., Tič, V. (2019). Excellent lubricating properties of ionic liquid - myth or truth. Serbiatrib '19 - 16th International Conference on Tribology, Kragujevac. Serbia. ISSN 2620-2832, Vol. 1. No. 1. University of Kragujevac. Faculty of engineering. 555-562.
- [9] Kambič, M., Kalb, R., Tašner, T., Lovrec, D. (2014). High Bulk Modulus of Ionic Liquid and Effects on Performance of Hydraulic System, The scientific world journal, ISSN 1537-744X. Vol. 2014. Art. No. 504762. 1-10, doi: 10.1155/2014/504762.
- [10] Tič, V., Manhartsgruber, B., Gubeljak, N., Lovrec, D. (2018). Low compressibility of ionic liquids and its effects on pulsation within hydraulic system. 11th International Fluid Power Conference, Vol. 1. Aachen. Germany. 486-493.
- [11] Lovrec, D. (2017). Filterability of ionic liquid used as a hydraulic fluid. The 5th Virtual Multidisciplinary Conference QUAESTI. Zilina, Slovak Republic. ISSN 2453-7144. Vol. 5. Iss. 1. EDIS - Publishing Institution of the University of Zilina. 160-164.
- [12] Lovrec, D., Tič, V. (2020). Ionic liquids as wide operating temperature range lubricant. New technologies, development and application III, Sarajevo, Bosnia and Herzegovina. ISSN 2367-3370. Vol. 128). Cham: Springer. cop. 2020. Vol. 128. 348-359.
- [13] Kambič, M., Kalb, R., Tič, V., Lovrec, D. (2018). Compatibility of ionic liquids with hydraulic system components. Advances in production engineering & management, ISSN 1854-6250. Vol. 13. No. 4. 492-503. doi: 10.14743/apem2018.4.306.
- [14] Kambič, M., Lovrec, D. (2017). Problems of testing new hydraulic fluids. Internal conference Fluid Power 2017. Conference proceedings. 1st ed. Maribor. University of Maribor Press. 281-293.
- [15] Lovrec, D., Tič, V. (2021). A new approach for long-term testing of new hydraulic fluids. New technologies, development and application IV, International Conference New Technologies, Development and Application. Sarajevo. Bosnia and Herzegovina. ISSN 2367-3370. Vol. 233. Cham: Springer Natur. cop. 2021. 788-801.
- [16] Lovrec, D. (2018), Ionic liquids vs. conventional hydraulic oils a comparison of properties and challenges. TMT 2018 - 21st International Research/Expert Conference "Trends in the Development of Machinery and Associated Technology", Karlovy Vary. Czech Republic. ISSN 1840-4944. Year 21. No. 1.: University of Zenica. 73-76.
- [17] Lovrec, D., Kalb, R., Tič, V. (2020). Basic aspects when using ionic liquids as a hydraulic fluid. 12th International Fluid Power Conference - 12. IFK, Dresden. Vol. 1. Technische Universität Dresden. 273-282.